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A Working Party Report on

Control of Corrosion in Cooling Waters

Edited by J. D. Harston and F. Ropital



M A N E Y

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European Federation of Corrosion Publications

Series Introduction

The EFC, incorporated in Belgium, was founded in 1955 with the purpose of promoting European co-operation in the fields of research into corrosion and corrosion prevention.

Membership of the EFC is based upon participation by corrosion societies and committees in technical Working Parties. Member societies appoint delegates to Working Parties, whose membership is expanded by personal corresponding membership.

The activities of the Working Parties cover corrosion topics associated with inhibition, education, reinforcement in concrete, microbial effects, hot gases and combustion products, environment sensitive fracture, marine environments, refineries, surface science, physico-chemical methods of measurement, the nuclear industry, the automotive industry, computer based information systems, coatings, tribo-corrosion and the oil and gas industry. Working Parties and Task Forces on other topics are established as required.

The Working Parties function in various ways, e.g. by preparing reports, organising symposia, conducting intensive courses and producing instructional material, including films. The activities of the Working Parties are co-ordinated, through a Science and Technology Advisory Committee, by the Scientific Secretary. The administration of the EFC is handled by three Secretariats: DECHEMA e.V. in Germany, the Société de Chimie Industrielle in France, and The Institute of Materials, Minerals and Mining in the United Kingdom. These three Secretariats meet at the Board of Administrators of the EFC. There is an annual General Assembly at which delegates from all member societies meet to determine and approve EFC policy. News of EFC activities, forthcoming conferences, courses, etc. is published in a range of accredited corrosion and certain other journals throughout Europe. More detailed descriptions of activities are given in a Newsletter prepared by the Scientific Secretary.

The output of the EFC takes various forms. Papers on particular topics, for example, reviews or results of experimental work, may be published in scientific and technical journals in one or more countries in Europe. Conference proceedings are often published by the organisation responsible for the conference.

In 1987 the, then, Institute of Metals was appointed as the official EFC publisher. Although the arrangement is non-exclusive and other routes for publication are still available, it is expected that the Working Parties of the EFC will use The Institute of Materials, Minerals and Mining for publication of reports, proceedings, etc. wherever possible.

The name of The Institute of Metals was changed to The Institute of Materials on 1 January 1992 and to The Institute of Materials, Minerals and Mining with effect from 26 June 2002. The series is now published by Maney Publishing on behalf of The Institute of Materials, Minerals and Mining.

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Preface

The joint CEFRA COR — SCI commission 'Corrosion in the chemicals industry' has undertaken the task of developing corrosion prevention tools for chemical engineers. A number of working groups have been set up to treat subjects of general interest, and studies have already been published on the degradation of fluorinated polymers and corrosion beneath insulation. The present treatise on the control of corrosion problems in cooling waters forms part of this work.

The question of water treatment is a difficult problem, due to the many types of water of different origin, and the various uses to which they are put. The aim of this guide is to outline the fundamental characteristics of waters and the various means of treatment made available by the sub-contractors who generally install factory water networks.

For proper management of these utilities it is essential that those responsible for operating them have a basic knowledge of the principles of water treatment, in order to understand the factors involved and, if necessary, to communicate effectively with suppliers.

The following people have actively contributed to the present work: Sylvain Audisio (I.N.S.A., Lyon), Marie-Claude Bonnet (E.P.I.), Sophie Blagojevic (Total), Jean-Louis Crolet (Total), Jean-Marie Daubenfeld (AtoFina), Elisabeth Doyelle (Total), Pierre Eichner (Rhône Poulenc Industrialisation) and Jean Ledion (E.N.S.A.M., Paris).

All those who have given their time and shared their knowledge are warmly thanked for their enthusiasm and participation.

Jean Goudiakas (AtoFina)

Foreword

The control of corrosion in cooling water systems is a major challenge for the refinery and petrochemical industries in Europe and all over the world.

The objectives of working groups such as the CEFRA COR group 'Corrosion in the Chemical Industries' and the European Federation of Corrosion (EFC) group WP15 'Corrosion in the Refinery Industry' are to provide improvement of knowledge and recommendations on specific corrosion problems such as the topic of this EFC publication 'Control of Corrosion in Cooling Waters'. The present document is the synthesis of much work and exchange of experience: we are confident that the information will form a sound basis for many people involved with corrosion management in this area.

We want to thank Jean Goudiakas and the CEFRA COR group for their enormous effort in writing such a guideline. Our thanks also go to the EFC WP15 working group and especially to Wim Verstijnen, Terry Hallett and Hennie De Bruyn for assistance with reviewing this document.

John Harston François Ropital
EFC WP15 Chairmen

1

Introduction

In cooling water circuits, corrosion and scaling problems are not new, but continuing trends in environmental legislation are leading to ever greater degrees of evaporation and consequently to very high residual concentrations of various species. Thus, even if the waters used are initially clean and non-corrosive, because of this concentration effect, they become corrosive and their tendency to induce scaling and biofouling increases.

Faced with this situation, those responsible for water treatment tend to respond on a case-by-case basis, leading to a wide variety of treatments. However, the circuit operator, who pays for these treatments, must be able to assess their validity. This is the purpose of the present guide, which endeavours to describe in clearly understandable terms what happens in the water as it becomes more concentrated, and what occurs during the different treatments to which it is subjected. It is then possible to consider the interaction between a particular water and the materials with which it is in contact. This is the problem of 'corrosivity', which must be clearly distinguished from that of 'aggressivity' (with respect to marble).

It is emphasised that the design, the conditions of construction and the mode of operation of a plant can often be much more important than the composition of the circuit feed water.

Readers will discover that all the theoretical background necessary to understand what goes on within cooling circuits has given rise to methods for evaluating both corrosion and scaling. They will then be in a position to enter effectively into dialogue with their water treatment providers, and the aim of the present guide will have been achieved.

N.B.: All the figures quoted in this document are given on a purely indicative basis.

2

The Circuits

The aim of cooling circuits is to remove heat generated by some industrial process. Water is the cooling fluid most commonly employed for this purpose. The nature of the materials used to construct the circuit and the vessels to be cooled (condensers, heat exchangers, fluid refrigerators, motors, reactors, furnaces, etc.) is extremely varied.

Three categories of cooling circuits can be distinguished:

2.1. Once-through Cooling Systems

In these circuits, water is pumped from the natural surroundings and is returned there after a single passage through the cooling system. The circuit is characterised by a cooling water flow rate (D) and by the difference in temperature between the inlet and outlet of the apparatus to be cooled.

2.2. Closed Recirculating Systems

In a closed circuit, all the cooling water is confined in a closed loop. There is no contact with the atmosphere and therefore no risk of contamination by the latter. Heat is removed by conduction and convection via a secondary circuit (semi-open circuit, refrigerator unit, etc.) and not directly by evaporation of the primary circuit water. Evaporation is thus virtually non-existent and renewal of the water is usually associated with maintenance or other operations that require partial draining of the circuit. For operational reasons, it is often useful to incorporate a slipstream filtration system.

Closed circuits can only be used in small-sized plants, in high flow rate systems, or in systems with a refrigeration unit (iced water tank).

2.3. Open Recirculating Cooling Systems

This type of circuit is the most widely used. The semi-closed circuit is fed by a feed-water supply A . The circulating water flow rate D is maintained constant by pumps. The water is heated by the hot process fluid in the heat exchangers. The hot water is in direct contact with the air in the cooling towers, and is cooled both by this contact and by loss of latent heat of evaporation. Water losses due to evaporation E_v and droplet entrainment E_i must be compensated. The evaporated water can be considered to be practically completely demineralised. Simple compensation for this water by a corresponding addition of raw feed water would lead to an increasing concentration of dissolved salts, which would rapidly reach

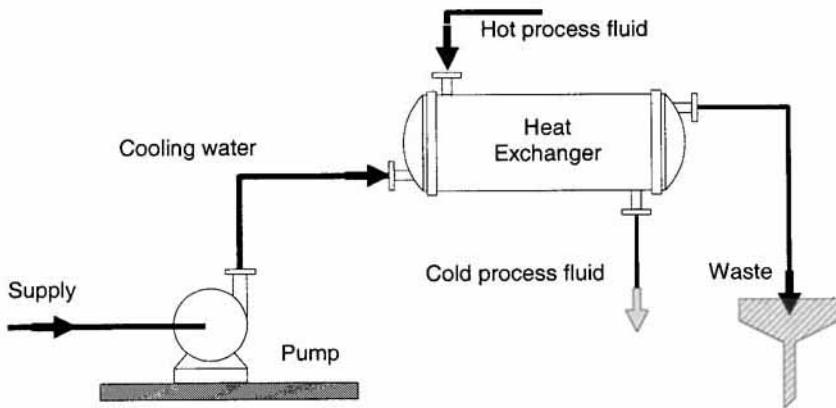


Fig. 1 Once-through cooling system.

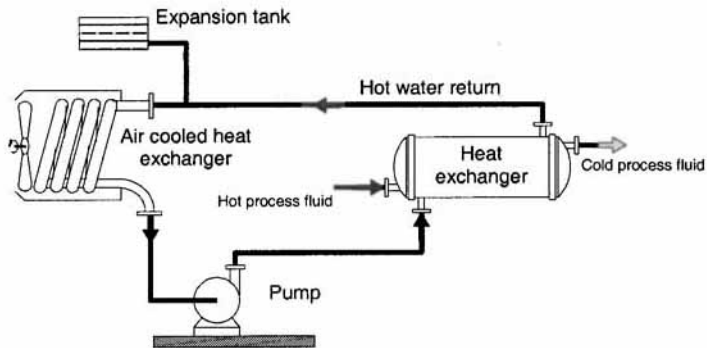


Fig. 2 Closed recirculating cooling system.

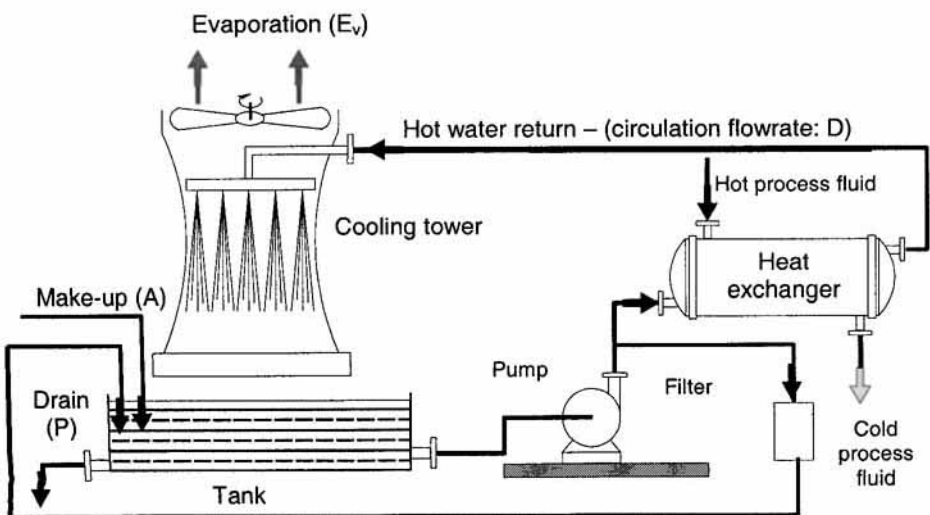


Fig. 3 Open recirculating cooling system.

their solubility limit. Partial draining P is therefore necessary to achieve the desired concentration ratio R_c .

2.3.1. Evaporation

The relative evaporation rate E_v/D is the ratio between the latent heat of evaporation of the water lost and the sensible heat lost by the circulating water. It is therefore proportional to the difference in water temperature Δt between the inlet and outlet. In practice, it is considered that 1% of the circulating flow rate D is evaporated for each 5.6°C of temperature drop through the cooling tower:

$$E_v = D \left(\frac{\Delta t}{560} \right)$$

The extent of evaporation in a cooling tower is limited by the relative humidity of the air.

2.3.2. Droplet entrainment

Forced air ventilation leads to the loss of water in the form of fine droplets, some of which are entrained in spite of systems specially designed to eliminate them. The degree of entrainment depends on the type of cooling tower and is defined by the constructors. In general, entrainment losses E_t are estimated to represent 1/1000 of the circulating flow rate D .

$$E_t = \frac{D}{1000}$$

Entrainment losses can be reduced by the installation of drift eliminators. High efficiency versions can reduce this to 0.01% of the circulating flow D .

2.3.3. Concentration ratio

The concentration ratio R_c is defined from the total salinity S_t :

$$R_c = \frac{\text{Salt concentration in the circuit water}}{\text{Salt concentration in the feed-water}} = \frac{S_t \text{ of the circuit water}}{S_t \text{ of the feed-water}}$$

The concentration ratio can be limited by factors of two types:

Equipment-related factors:

- uncontrolled leaks in certain 'old' circuits;
- intense droplet entrainment.

Chemical factors:

Certain compounds, such as sulphates, can precipitate out if their concentration in the water becomes too high. It is therefore these compounds that limit the permissible salinity.

The permissible concentration ratio depends on the salinity of the feed-water. It is defined using methods such as calcium-carbonate species charts (Chapter 3). In order to maintain this ratio constant, the quantity of salts entering the circuit must be equal to that leaving it :

$$A.S_f \text{ (feed-water)} = P.S_t \text{ (circuit water)}$$

Useful formulae

$$P = \frac{A}{R_c}$$

$$A = E_c + E_t + P$$

$$P \cong \frac{E_v}{(R_c - 1)}$$

2.3.4. Cycle time and semi-residence time

The cycle time C is the time taken for the water to make a complete lap of the cooling circuit. It depends on the total volume V and the circulating flow rate D :

$$C = \frac{V}{D}$$

The semi-residence time or half-life ($t_{1/2}$) represents the time necessary for the initial concentration (C_0) of a substance injected at time (t_0) to be reduced by half:

$$t_{1/2} = \left(\frac{V}{P} \right) \log 2 \cong 0.7 \left(\frac{V}{P} \right)$$

NB: This concept is important for water treatment, particularly with biocides.

2.3.5. Types of cooling tower

In cooling towers, the water is cooled by intimate contact with air. The towers are classified in different categories:

- cascade types, in which the water is fed to a distribution ramp at the top of the tower, and overflows onto a series of slats;
- spray types, in which the water is atomised under pressure at the top of the tower;

- honeycomb types, in which the water is first atomised and then falls through a honeycomb structure that enhances the contact between the water droplets and air;
- streaming types, in which the cooling water streams down the outside of heat exchanger tubes containing the hot process fluid.

Depending on the design and size of the plant, the air flow may be forced or may be ensured by natural draught, due to the temperature gradient in the tower.

2.3.6. Diverted stream filtration

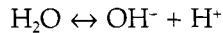
Slipstream filtration is required when the feed-water is contaminated (e.g. water recycled after biological treatment) and/or when the residence time in the circuit is long. The diverted flow rate generally represents about 5% of that circulating in the circuit. Mineral or organic suspended solids are removed by filtering through sand or a membrane or some equivalent system. The concentration of suspended solids SS can be maintained less than 10 mg L^{-1} , sometimes enabling a higher concentration ratio R_c to be tolerated.

3

The Water

3.1. Physical Properties

The density of water is a maximum at 4°C, equivalent to 0.99997 g cm⁻³, rounded off to 1.00000. Water has a slight electrical conductivity, related to the fact that it is partially ionised:



$$K = (\text{OH}^-) (\text{H}^+) = 10^{-14} \text{ at } 20^\circ\text{C}$$

where K is the ion-product constant; (X) is the thermodynamic activity of the component X ; assimilated to a first approximation to its molar concentration. By definition

$$\text{pH} = -\log(\text{H}^+)$$

The pH varies with temperature. For high purity water, pH = 7.0 at 20°C, 6.6 at 50°C and 6.1 at 100°C. Natural waters have pH values between 5 and 9 at 20°C, while a 0.1 N solution of sulphuric acid has a pH of 1.2.

3.2. Thermal Properties

Table 1. Thermal properties of water

Property	Value in usual units
Latent heat of melting	334 kJ kg ⁻¹
Melting point	0°C (insensitive to atmospheric pressure)
Boiling point	100°C at 760 mm of Hg (varies with pressure)
Latent heat of evaporation	2255 kJ kg ⁻¹ at 20°C
Specific heat of liquid water	4.184 kJ kg ⁻¹ °C ⁻¹

3.3. Water Sources

Waters used for industrial cooling have various origins, the principal types being:

- well waters/subterranean waters;
- surface waters;
- recycled waters: recovery of waste waters, rainwater, etc.

Depending on the type of source and the region of origin, the water characteristics can vary enormously. Well waters have relatively stable properties, whereas surface (river) waters have variable characteristics, depending on the local climate, and their use poses certain problems. There is an increasing tendency to use 'recycled' waters for cooling circuits, with generally high salinity and the presence of suspended mineral and organic matter, together with various other contaminants.

3.4. Compositions of Natural Waters

3.4.1. Dissolved matter

'Pure' water does not exist naturally, since water is an excellent solvent for many substances. Natural water thus contains mineral salts in solution (salinity), together with gases and organic species.

Dissolved salts

The mineral salts present in water vary greatly according to the region of origin. In an electrolyte like water, these salts dissociate into their respective cations and anions.

Dissolved gases

The dissolved gases are essentially :

- oxygen (concentration at 20°C about 8.8 ppm);
- carbon dioxide;

Table 2. Typical anions and cations dissolved in water

Cations	Anions
Na ⁺	HCO ₃ ⁻
Mg ²⁺	CO ₃ ²⁻
Ca ²⁺	OH ⁻
K ⁺	Cl ⁻
Fe ²⁺ or Fe ³⁺	SO ₄ ²⁻
H ⁺	NO ₃ ⁻
	PO ₄ ³⁻ , HPO ₄ ²⁻ , H ₂ PO ₄ ⁻
	SiO ₃ ²⁻

- nitrogen;
- possibly NH_3 and H_2S .

3.4.2. Suspended solids and colloidal solutions

Suspended solids can be extremely variable, including quartz particles from clays, organic particles, plant debris and living organisms (bacteria, zooplankton and phytoplankton).

In terms of size, dissolved species are generally smaller than 1 nm, while colloidal suspensions range from 1 nm to 1 μm and suspended particles are larger than 1 μm .

3.5. Chemical Analysis of Water

3.5.1. Measurement units

Gram equivalents

A gram equivalent is the molecular weight of an ion divided by its valency.

Milliequivalents per litre (meq L^{-1})

This is an extremely practical unit of concentration, equal to one thousandth of a gram equivalent per litre. Whatever the salt dissolved, the concentrations of the cation and anion are the same when expressed in meq L^{-1} . Similarly, in a complex solution, the sum of the anion concentrations is equal to the sum of the cation concentrations.

Other units (°f)

The French degree ($1^\circ\text{f} = 0.2 \text{ meq L}^{-1}$) is another unit commonly used in France to express ionic concentrations, and often leads to integral numbers rather than decimals. There is also a German degree (1°dH corresponds to 10 mg CaO L^{-1} of water), while in the USA, concentrations are sometimes expressed in mg L^{-1} of calcium carbonate, since the latter has a molecular weight of 100 and a gram equivalent of 50.

Table 3 gives an example of a water analysis expressed in different units.

Table 3. Example of a water analysis expressed in different units

Cations					Anions				
	mg L^{-1}	meq L^{-1}	mg $\text{CaCO}_3 \text{ L}^{-1}$	°f		mg L^{-1}	meq L^{-1}	mg $\text{CaCO}_3 \text{ L}^{-1}$	°f
Ca^{2+}	113	5.65	282	28.2	Cl^-	57	1.61	80.4	8.0
Mg^{2+}	28.5	2.34	117	11.7	SO_4^{2-}	142	2.96	148	14.8
Na^+	36.5	1.59	79.3	7.93	SiO_3^{2-}	7.1	0.19	9.3	0.9
					HCO_3^-	317	5.20	260	26

3.5.2. Principal parameters and definitions

For cooling circuit waters the criteria detailed in Table 4 are defined:

3.5.3. Concepts of temporary and permanent hardness

The permanent hardness TH_p of a water is the hardness not associated with carbonates or bicarbonates, and corresponds to the calcium and magnesium ions balanced with chlorides, sulphates, nitrates, etc. The temporary hardness TH_t

Table 4. Water criteria

Parameter	Definition	Standard	Usual units
pH	Hydrogen potential	ISO 10523	
Electrical conductivity or resistivity		NF EN 27888	Siemens cm^{-1} or ohm.cm
SS	Suspended solids	NF EN 872	mg L^{-1}
TH	Total hardness (Ca and Mg)	ISO 6058	meq L^{-1}
HCa	Hardness (Ca only)	ISO 6059	meq L^{-1}
MA	M-Alkalinity ($\text{OH}^- + 0.5\text{CO}_3^{2-} + 0.33\text{PO}_4^{3-}$)	NF EN 9963	meq L^{-1}
PA	P-Alkalinity ($\text{OH}^- + \text{CO}_3^{2-} + \text{HCO}_3^- + 0.66\text{PO}_4^{3-}$)	NF EN 9963	meq L^{-1}
BOD 5	Biochemical oxygen demand after 5 days	ISO 5815	$\text{mg O}_2 \text{ L}^{-1}$
COD	Chemical oxygen demand	NF T 90-101	$\text{mg O}_2 \text{ L}^{-1}$
TOC	Total organic carbon	NF EN 1484	mg C L^{-1}
NH_4^+	Ammoniacal nitrogen	NF T 90-015	mg L^{-1}
Kjeldahl nitrogen (NTK)	Ammoniacal nitrogen + part of the organic nitrogen	NF EN 25663	mg L^{-1}
Various anions	Ion chromatography measurement of F^- , Cl^- , NO_3^- , NO_2^- , PO_4^{3-} , Br^- , SO_4^{2-}	NF EN ISO 10304-1	mg L^{-1}
P	Phosphorus	NF EN 1189	mg L^{-1}
Metals (33 elements)	Ag, Cd, Cu, Co, Cr, Fe, Mn, Ni, Pb, Zn, ...	ISO 11885	mg L^{-1}
Cl^-	Chloride ions	ISO 9297	mg L^{-1}
SO_4^{2-}	Sulphate ions	ISO 9280	mg L^{-1}
NO_3^-	Nitrate ions	ISO 7890	mg L^{-1}
SiO_2	Silica	NF T 90-045	mg L^{-1}
Total bacteria	Enumeration of micro-organisms by culture	ISO 8199	CFU mL^{-1} (CFU = Colony Forming Unit)
Sulphate and thiosulphate reducing bacteria (SRB/TRB)	Anaerobic bacteria that reduce either sulphates or thiosulphates respectively, liberating sulphide ions.		CFU mL^{-1}
AOX	Adsorbable organic halogen	NF EN 1485	mg L^{-1}

Table 5. Relationships between PA and MA

Dissolved ion	PA = 0	PA < MA/2	PA = MA/2	PA > MA/2	MA = PA
OH ⁻	0	0	0	2PA - MA	PA
CO ₃ ²⁻	0	2PA	MA	2(MA - PA)	0
HCO ₃ ⁻	MA	MA - 2PA	0	0	0

corresponds to the calcium and magnesium ions balanced with carbonate and bicarbonate ions.

$$TH_t = TH - TH_p$$

where TH = total hardness.

3.5.4. Relationships between M- and P-alkalinity

M-alkalinity (MA) measures the amount of carbonate, bicarbonate and hydroxide present based on a sulphuric acid titration using a methyl orange indicator. P-alkalinity (PA) measures the amount of carbonate and hydroxyl alkalinity based on a sulphuric acid titration using a phenolphthalein indicator.

The relative values of MA and PA can be used to calculate the concentrations of hydroxide, carbonate and bicarbonate ions in the water. The correspondence with the water constituents is summarised in Table 5, where phosphate ions have been neglected.

3.6. The Behaviour of Water

3.6.1. The decisive role of carbonic species

The carbonic species present in water are often improperly termed 'inorganic carbon'. They include dissolved CO₂ and bicarbonate (HCO₃⁻) and carbonate (CO₃²⁻) ions. The dissolved carbon dioxide partially reacts with water to form carbonic acid (H₂CO₃) and these two species together represent the free CO₂:

$$[\text{CO}_2 \text{ free}] = [\text{CO}_2 \text{ dissolved}] + [\text{H}_2\text{CO}_3]$$

The total CO₂ is given by

$$[\text{CO}_2 \text{ total}] = [\text{CO}_2 \text{ free}] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]$$

The concentrations of these species are determined by the first and second carbonic acid dissociation equilibria and their corresponding mass action laws, and by the solubility equilibrium of calcium carbonate:

These equations can be used to calculate the concentrations of bicarbonate and carbonate as a function of the pH and the total dissolved CO₂. It is found that:

	Equilibrium	Equilibrium constant (25°C)
Reaction of CO ₂ with H ₂ O	CO _{2 dissolved} + H ₂ O ⇌ H ₂ CO ₃	$\frac{[H_2CO_3]}{[CO_{2\ dissolved}]} = K_h$
1st dissociation of H ₂ CO ₃	H ₂ CO ₃ ⇌ H ⁺ + HCO ₃ ⁻	$\frac{[H^+][HCO_3^-]}{[H_2CO_3]} = K_c$
other form	CO _{2 free} + H ₂ O ⇌ H ⁺ + HCO ₃ ⁻	$\frac{[H^+][HCO_3^-]}{[CO_{2\ free}]} = K_1 \approx 10^{-6.5}$
2nd dissociation of H ₂ CO ₃	HCO ₃ ⁻ ⇌ H ⁺ + CO ₃ ²⁻	$\frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} = K_2 \approx 10^{-10}$
Solubility of CaCO ₃	Ca ²⁺ + CO ₃ ²⁻ ⇌ CaCO ₃	$[Ca^{2+}][CO_3^{2-}] = K_s$

- for pH<4, all is in the form of CO_{2 free}, that is CO_{2 dissolved} and H₂CO₃;
- for 4≤pH≤8.2, the quantity of carbonate is negligible, and the pH is controlled by the carbonic acid/bicarbonate buffer;
- for 8.2<pH≤12.5, the pH is controlled by the bicarbonate/carbonate buffer.

The gradual change from one control regime to the other is illustrated graphically in Figure 4.

3.6.2. Equation of electrical neutrality

In the water, the sum of the positive ionic charges is equal to the sum of the negative ionic charges. When the concentrations are expressed in mmole L⁻¹, the electrical neutrality equation is:

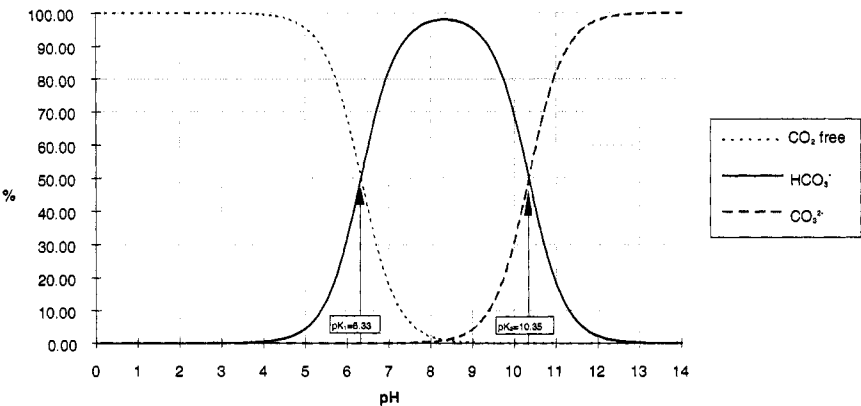
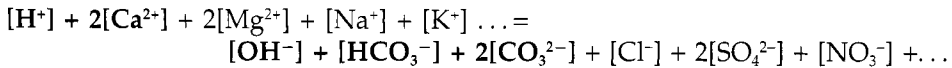
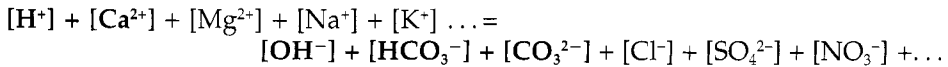


Fig. 4 Carbonic species as a function of pH.



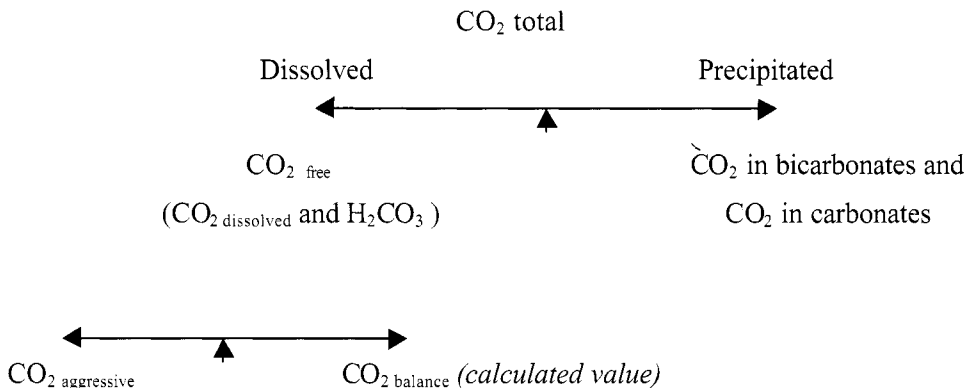
In meq L⁻¹, this becomes:



The species in bold type are those involved in the calcium-carbonic species equilibria described above. They are sometimes termed 'fundamental species'. This equation can be used to calculate the pH as a function of the fundamental species present (see Appendix A).

3.6.3. Concept of aggressive water

Depending on the pH and the water composition, calcium carbonate may be precipitated or dissolved. In the first case, it is a 'scaling' water, while in the second, it would be described as 'aggressive' in the old tests where the behaviour was revealed by the effect on a sample of marble.



- If the water is in carbonate/carbonic species equilibrium, $\text{CO}_{2 \text{ free}} = \text{CO}_{2 \text{ balance}}$.
- If $\text{CO}_{2 \text{ free}} > \text{CO}_{2 \text{ balance}}$, the water is undersaturated with respect to CaCO_3 , and is therefore aggressive. The CO_2 is then sometimes called $\text{CO}_{2 \text{ aggressive}}$.
- If $\text{CO}_{2 \text{ free}} < \text{CO}_{2 \text{ balance}}$, the water is supersaturated with respect to CaCO_3 , and scaling may occur. The water can produce a calcium carbonate scale.

In order to evaluate the carbonate/carbonic species equilibrium and the risk of scaling, most companies use more or less approximate or empirical methods (Langelier, Ryznar, Stiff and Davis, Hallopeau Dubin, Pourbaix, Rocques). These methods should normally disappear and be replaced by more rigorous and universal techniques, such as that due to Legrand-Poirier, which are now very simple to use due to the availability of new computer software (some of these methods are described in Appendix A).

4

The Principal Problems Arising from the Use of Untreated Water

There are three major types of problem in cooling water circuits:

- scaling;
- corrosion;
- fouling, particularly the formation of biofilms.

In practice, these problems are often strongly interrelated and corrective actions taken to treat one of them frequently have repercussions on the others.

4.1. Scaling

4.1.1. Introduction

Scaling is considered to occur when a metallic or other surface becomes covered by an adherent mineral deposit. The distinguishing feature compared to a deposit produced by the sedimentation of solid particles from the liquid is the fact that the scale adheres to the surface. Scale deposits can enhance trapping of suspended solids.

In a water fed cooling circuit, scaling is essentially due to the formation of calcium carbonate. The scale may subsequently contain other substances, such as clays, algae residues, or calcium sulphate, but it is always calcium carbonate that precipitates first, since its solubility is lower than for the other species liable to appear in this type of water.

4.1.2. Nucleation and growth of deposits on walls

In the case of both metal and polymer walls, the first nuclei formed serve as sites for subsequent precipitation, so that the CaCO_3 deposit grows out from them. Once the surface is completely covered, the behaviour is the same whatever the nature of the wall. When the water contains relatively little suspended solids, the calcium carbonate layer continues to serve as a precipitation site and can also electrostatically trap sufficiently fine CaCO_3 nuclei formed in the liquid. The deposit continues to grow in this manner.

4.1.3. Kinetics of scaling

In practice, various materials are present in the circuit. Heat exchangers are generally constructed from metals and alloys, whereas cooling towers contain

many polymer exchange surfaces. Several mechanisms can therefore occur simultaneously. The calcium carbonate may have several forms:

- electrically charged colloidal nuclei;
- nuclei that have grown to crystallites capable of settling out as sludges in turbulence-free zones;
- adherent scale on walls.

A more detailed description of scaling kinetics is given in Appendix B.

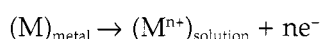
4.1.4. Interfering factors

Suspended solids, algae, metal ions and oxidising agents interfere with scaling, exerting either an inhibiting or a stimulating influence, depending on the plant operating conditions. There are many different theories concerning the mechanisms involved and no clear picture has yet emerged.

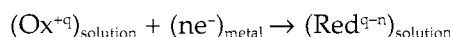
4.2. Corrosion

4.2.1. Summary of principles

Aqueous corrosion of metals is electrochemical in nature and involves two independent reactions, corresponding to oxidation of the metal and reduction of some species in the corrosive medium. The metal oxidation reaction is 'anodic' and releases positively charged metal ions into the solution and electrons into the metal:



The electrons liberated in the metal reduce an oxidant in the corrosive medium in the 'cathodic' reaction:



The most common oxidants are :



In natural water, the H^{+} concentration is related principally to the amount of dissolved CO_2 , via the first carbonic acid dissociation reaction.

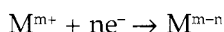


The oxygen concentration of a water depends both on its origin and the type of circuit concerned. In fact, oxygen has two effects, acting both as an

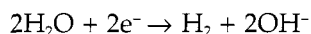
electrochemical oxidant in the corrosion reaction and as a chemical oxidant in the conversion of the primary corrosion products (e.g. oxidation of Fe^{2+} to Fe^{3+}).

To prevent all risk of corrosion 'by oxygen', boiler waters are treated to remove it by deaeration, deactivation, thermal degassing or the addition of specific reagents (sulphites, hydrazine, etc.). At the present time, this procedure is not applied in open recirculating cooling water systems.

(3) multivalent metal ions:



(4) the water itself:



On a macroscopic scale, the overall corrosion may be uniform, with no apparent net current, or may be heterogeneous, with currents flowing between local anodes and cathodes. In certain cases, the corrosion may be completely confined to local regions (e.g. pitting and crevice corrosion).

A corrosion inhibitor is a substance that reduces the rate of either the anodic or the cathodic reaction, the most effective ones acting on both of them ('mixed' inhibitors). So-called 'anodic' inhibitors have a greater effect on the anodic reaction. Although they can be extremely efficient, there is the risk that a local loss of inhibition may lead to catastrophic pitting attack.

4.2.2. Factors involved in corrosion

Table 6. *Factors involved in corrosion*

Physical-chemical factors	• Reactant concentrations • Oxygen, dissolved salt, SS and micro-organism contents • Acidity of the medium (pH) • Temperature, pressure
Metallurgical factors	• Alloy composition • Processing route • Alloy impurity levels • Heat treatment and thermomechanical processing cycles • Joining processes
Factors defining the service conditions	• Surface condition • Velocity • Suspended solids • Protective coatings • Component geometry • Mechanical loading conditions • Use of inhibitors
Time dependent factors	• Aging • Mechanical loads • Temperature • Modifications in protective coatings

4.2.3. Types of corrosion

A wide variety of corrosion modes can occur, depending on the medium and materials concerned. The reader is referred to recent general textbooks and papers on corrosion.

4.2.4. Common materials used and associated water corrosion problems

Table 7.

Principal corrosion modes	Parameters related to		
	the medium	the material	the plant
Unalloyed steels and cast irons			
Uniform	pH, dissolved oxygen, temperature		
Pitting	pH, oxidant	Inclusion content	
Crevice	pH, oxygen, chlorides, deposits, SS		Confinement
Selective (graphitisation of cast irons)	pH	Lamellar graphite structures	Confinement
Galvanic			Contact with copper, stainless steel
Galvanised steel			
Uniform	acid pH, oxygen, aggressive water $\text{TH} < 2 \text{ meq L}^{-1}$		Stagnant conditions in weld zones
Pitting (pustules)	Copper ions, temperatures $> 60^\circ\text{C}$	Inclusion content	Threaded zones
Crevice	pH, oxygen, chlorides, deposits		Confinement, threaded zones
Stress corrosion cracking	OH^- , NO_3^-		Tensile stresses
Stainless steels			
Crevice	Deposits, biofilms		Confinement (joints)
Pitting	pH, chlorides, reduced forms of sulphur, biofilms	Inclusions, scratches, soiling	
Intergranular		Weld zones	Overheating during welding, poorly quenched castings
Erosion/cavitation	SS, gas bubbles		Flow rate in pumps (depending on the alloy)
Stress corrosion cracking	pH, chlorides		Temperatures $> 50^\circ\text{C}$, tensile stresses (created during fabrication, e.g. welding)

Table 7. Continued

Principal corrosion modes	Parameters related to		
	the medium	the material	the plant
Nickel base alloys			
Uniform	Aeration, oxidant	Cr-free alloys	
Intergranular		Fe-free alloys	As for stainless steels
Crevice	Biofilms, deposits		Low flow rates
Aluminium and its alloys			
General	pH<4 and pH>9		
Selective (exfoliation)	pH	2000, 5000 and 7000 series (intermetallic precipitates)	Acceleration by galvanic coupling
Crevice	SS, biofilms		
Pitting	pH, aeration	Alloying elements	Contact with copper or other more noble materials
Galvanic	Conductivity, chlorides		
Intergranular		Nature of alloying additions and intermetallic phases	
Stress corrosion cracking	Chlorides, pH, aeration	Many metallurgical parameters	Tensile stresses
Copper			
Uniform	pH<4, amines and/or ammonium ions (blue water formation), sulphides		
Type 1 pitting		Annealed copper with carbon-containing residues or copper oxides	Cold circuits
Type 2 pitting	Low TH, $\text{HCO}_3^-/\text{SO}_4^{2-}<1$		Hot circuits
Crevice	Deposits, biofilms		Presence of steel with release of Fe^{3+} ions
Erosion			Flow velocities $>1 \text{ m s}^{-1}$
Stress corrosion cracking	Amines, ammonium ions		Tensile stresses
Galvanic	• Coupling with steel (chicanes) • Brazed joints (copper/phosphorus)		High circuit temperatures($>50^\circ\text{C}$)

Table 7. Continued

Principal corrosion modes	Parameters related to		
	the medium	the material	the plant
Copper alloys			
Selective :			
• Dezincification of brasses		Nature and concentration of alloying elements	
• Al depletion of Cu-Al alloys		Heat treatment	
• Ni depletion of Cu-Ni alloys	Excess sulphite	Brazing	Expansion tanks open to the atmosphere
Erosion			Flow velocity (critical value for a given alloy)
Stress corrosion cracking	Amines, ammonium ions	Nature and concentration of alloying elements	Tensile stresses generated during fabrication
Crevice	Deposits, biofilms		Confinement

4.3. Corrosion and fouling induced by micro-organisms

Micro-organisms are present naturally in virtually all waters and if they proliferate too rapidly they can create two types of problem in water circuits:

- 'biofouling', corresponding to the accumulation of micro-organism colonies on equipment surfaces, leading to the formation of 'biofilms';
- 'biocorrosion', corresponding to chemical attack by micro-organisms. In the case of metals, the corrosion is generally due to bacteria.

In both cases, the consequences of the proliferation of micro-organisms can be important, with loss of efficiency of heat exchangers, obstruction of piping, increased back pressures and even leakage by breakthrough corrosion.

4.3.1. Micro-organisms in water circuits

4.3.1.1. General aspects.

The micro-organisms encountered in cooling circuits are essentially of three types, namely, bacteria, algae and fungi. However, to complete the description of biofouling, the case of macrofouling by higher organisms, such as mussels and other molluscs, particularly in circuits fed by seawater, must also be mentioned.

Bacteria

Bacteria are unicellular organisms, from 0.1 to 100 μm in size, which multiply extremely rapidly. They draw the energy required for their development from the oxidation or reduction of certain compounds.

Among the multitude of species of bacteria, only a few are responsible for biocorrosion and biofouling phenomena. The bacteria encountered in water circuits can be classified in two categories:

- aerobic bacteria, which need oxygen to proliferate;
- anaerobic bacteria, which can proliferate only in the absence of oxygen, and are generally found in confined zones, beneath deposits, etc.

Algae

Micro-algae produce their energy by photosynthesis and require light, air and water to develop. In water circuits, they are encountered mainly in zones exposed to the atmosphere, such as tanks, cooling towers, etc.

Fungi

Although often considered to belong to the plant kingdom, fungi do not possess chlorophyll and therefore cannot obtain energy by photosynthesis. They thus require an organic source of carbon. They are frequently observed on wooden structures.

*4.3.1.2. Principal species responsible for biocorrosion and biofouling.***Ferrobacteria and manganobacteria**

Certain bacteria oxidise ferrous ions to ferric ions, while others oxidise manganous ions to manganic ions. In both cases, they make the medium more oxidising than in a sterile water. These bacteria are aerobic and produce large quantities of iron and manganese hydroxide sludges. In unalloyed steels and cast irons, the activity of ferrobacteria promotes pustule-type corrosion, particularly in the case of filamentary species such as *Leptothrix* and *Crenothrix*.

Bacteria with sulphur-based metabolisms

These include sulphate reducing bacteria (SRB), such as *Desulfovibrio*, *Desulfobacter*, etc., which reduce sulphates to sulphides and draw the energy required for their activity from the oxidation of short chain carbon compounds. They are therefore encountered beneath deposits, often in association with aerobic bacteria producing these compounds. The presence of other sludge-producing or pustule corrosion-inducing aerobic bacteria also promotes their development, by creating anaerobic niches. Their activity generally causes pitting. Some species stimulate the corrosion of ferrous materials by locally generating acidity and H_2S .

Other aerobic species of bacteria oxidise reduced forms of sulphur to sulphates and also generate sulphuric acid. They are most frequently observed in wastewater circuits, where their presence accelerates the degradation of concretes.

Bacteria with nitrogen-based metabolisms

These bacteria do not participate directly in the corrosion reactions, but can aggravate the attack in several ways:

- by oxidising ammonium ions to nitrites then nitrates, the associated drop in pH accelerating corrosion in numerous materials. However, the phenomenon is self-limiting, since when the pH falls below 5.8, the bacteria concerned (*Nitrosomonas*, *Nitrocystis*) become inactive;
- by oxidising nitrites used as corrosion inhibitors to nitrates (*Nitrobacter*, *Nitrocystis*);
- by producing ammonia, which is harmful towards copper alloys. However, ammonia-producing bacteria are relatively rare.

Bacteria producing organic sludges

In these aerobic bacteria, such as *Pseudomonas* and *Aerobacter*, the cell is surrounded by a thick film of polysaccharides. They generate large quantities of viscous and highly adherent sludge.

4.3.2. Biofilms

The micro-organisms in suspension and entrained by the water represent only a small fraction of the total microbial population. The bacteria rapidly colonise all surfaces in contact with the water, including clays, colloidal vegetable matter, steel walls, etc. Their adhesion is ensured by the secretion of organic macromolecules (exopolysaccharides — EPS), to form a biofilm. This film, which forms the interface between the water and the substrate, is composed of:

- 80 to 95% water;
- extracellular polymers (EPS) representing 85 to 98% of the organic matter;
- micro-organisms blocked in organic and mineral particles;
- substances adsorbed on the EPS or dissolved in the interstitial water;
- possible precipitated corrosion products.

A biofilm is thus far from being composed only of bacteria. Its thickness is the result of a dynamic equilibrium between growth and erosion. The films are neither uniform nor regularly distributed, due to:

- differences in local surface condition (weld zones, deposits, oxide scales, etc.);
- stratification, with aerobic species above and anaerobic species beneath deposits, the association of different bacteria composing an extremely efficient microscopic ecosystem;
- interweaving of such symbiotic systems to form a 'patchwork'.

For the micro-organisms concerned, the biofilm offers two essential advantages — it partially isolates them from the environment and traps chemical compounds that are indispensable for their development.

4.3.3. Conditions in the medium and microbial development

pH

For both bacteria and algae, the optimum pH conditions for growth are to either side of neutrality, with a range from 5 to 9 for bacteria. However, a few species can develop even outside of this range.

For fungi, the optimum pH is closer to 5.

Carbon-containing nutriments

Carbon-base compounds are necessary for cell construction and their oxidation is a source of energy for bacteria. For autotrophic bacteria, only CO₂ from the air is required, while heterotrophic bacteria use organic carbon. Some species, such as the sulphate reducing bacteria, can only metabolise short chain molecules, and for this reason, they are often found in association with aerobic bacteria.

Oxygen and other oxidants

Aerobic bacteria use atmospheric oxygen as an oxidising agent, while others use sulphur from sulphates or nitrogen from nitrates, reducing these substances to sulphides and nitrites respectively.

Nitrogen and phosphorus necessary for growth

Nitrogen present in oxidised form or in ammonium ions and phosphorus in the form of phosphates can be assimilated by the micro-organisms, particularly since only traces of these elements are required for their metabolisms.

Temperature

Temperature has a marked effect on the development of micro-organisms, each species of bacterium having an optimum range of temperature for growth (for many of them 35–40°C).

4.3.4. Biocides

Biocides are substances that are toxic for micro-organisms. Different biocides are required to treat fungi, algae and bacteria.

Fungicides are often based on heavy metals, such as lead, tin, and zinc, together with copper.

In the case of bacteria, a distinction must be made between bactericides and bacteriostatic reagents. Bactericides kill the bacteria, the 'minimum bactericide concentration' (MBC) being the dose necessary for a survival ratio of less than 1 in 10⁵. Bacteriostatic reagents inhibit the development of bacteria beyond a 'minimum inhibiting concentration' (MIC). In this case, the growth can revive as soon as the unfavourable conditions disappear.

4.4. Mechanisms and Aspects of Biocorrosion

The modifications made to a nominally sterile medium by the presence of micro-organisms can affect the corrosion resistance of all materials to a greater or lesser extent. The most serious situations are those leading to localised attack. However, a distinction must be made between cases where the bacteria simply cause a slight shift in the effects of corrosion controlling parameters and those where they produce a corrosive medium quite different from the original composition. Finally, in certain cases, the bacteria do not affect the corrosive medium directly but modify the corrosion inhibitors (e.g. consumption of nitrite inhibitors by bacteria with nitrogen-based metabolisms).

5

Treatment of Supply Waters

5.1. General Considerations

The purpose of feed-water treatments is to modify the properties of the raw water to meet the requirements of the circuit concerned. The type of treatment depends both on the quality of the feed-water and the intended application. The processes can be divided into three groups:

- those designed to treat suspended solids and colloidal solutions: coagulation, flocculation, settling and filtration;
- those for treating dissolved minerals: decarbonation, iron and manganese removal, softening and demineralisation;
- those used to remove organic matter and certain specific elements: oxidation and filtration.

5.2. Suspended Solids and Colloidal Solutions

In order to limit corrosion-erosion phenomena, levels of suspended solids have to be controlled (target < 20 ppm). The turbidity and colour of water are due essentially to the presence of very fine particles, often in the form of colloidal 'solutions'. These particles can remain in suspension for very long times and can often pass through very fine filters. In order to eliminate them, coagulation and flocculation techniques can be employed, the aggregated mass being readily removed by settling or filtration.

5.2.1. Coagulation

Preliminary coagulation removes the electric charges from the suspended particles, enabling them to coalesce. This is achieved by injecting and rapidly dispersing heavily charged ions. The principal coagulants employed are aluminium salts (chloride, polychloride, sulphate, and sodium aluminate), iron salts (ferric chloride, ferric and ferrous sulphates) and synthetic reagents.

The efficiency of coagulation is affected by pH, dissolved salts, water temperature and the type of coagulant. These factors, together with the complexity of the reactions involved, make it difficult to predict the optimum amount of coagulant, which must be determined experimentally.

5.2.2. Flocculation

The coalesced particles must continue to agglomerate into flaky aggregates or flocs. This is achieved by the use of additives called flocculants or flocculating agents. They are synthetic high molecular weight polyelectrolytes, which may be either electrically charged or neutral. The optimum type and concentration of flocculants are determined by testing.

5.2.3. Settling and flotation

Settling and flotation are used to separate suspended particles whose density is respectively higher or lower than that of water. Coagulation and flocculation affect these operations, since they change the physical properties of the particles (shape, size, density, rate of rise or fall).

NB The removal of the liquid from above the settled sediment is called decantation.

5.2.4. Filtration

Filtration is a physical process whereby suspended solids are removed from a liquid by passing it through a porous medium. The suspended solids are retained in or on the medium, which must therefore be cleaned regularly. This can be done either at predetermined intervals or automatically when the back pressure attains a certain level.

5.3. Dissolved Mineral Solids

5.3.1. Decarbonation with lime

Lime reacts with:

- carbonic species, forming insoluble calcium carbonates, which precipitate out;
- magnesium ions, forming magnesium hydroxide, which precipitates out;
- sulphates, forming calcium sulphate, which precipitates out.

All these reactions are slow at ambient temperature. They can be activated and taken to completion by either stirring, using a catalyst, or heating the water.

The permanent hardness associated with magnesium can be eliminated either by adding sodium carbonate with the lime used for decarbonation or by post-treatment with a cation exchange resin.

In theory, precipitation continues until the solubility limits for calcium carbonate and magnesium hydroxide are attained.

5.3.2. Softening

As the name implies, the aim of softening treatments is to remove the hardness from water. This is achieved by passing the water through a strong cation

exchange resin, which captures the alkaline earth elements and replaces them with sodium ions. The resin is regenerated with a solution of sodium chloride.

5.3.3. Demineralisation

5.3.3.1. With exchange resins.

Cations and anions are eliminated by passing the water through appropriate exchange resins and are replaced by H^+ and OH^- ions from the water. The cation resins are regenerated with acid and the anion resins with caustic soda.

Diagram 1 summarises the various exchanges involved.

The different kinds of resin beds can be combined in series in various ways, depending on the raw water and the final quality required. The beds may be in separate columns or in the same column. In the latter case they are called mixed beds.

Appendix C describes different possible combinations of ion exchange processes.

5.3.3.2. Membrane separation techniques.

These processes have developed considerably since the 1970s, due to the introduction of new high performance membranes. A membrane is a material in the form of a thin wall that has selective permeability to the different constituents of a

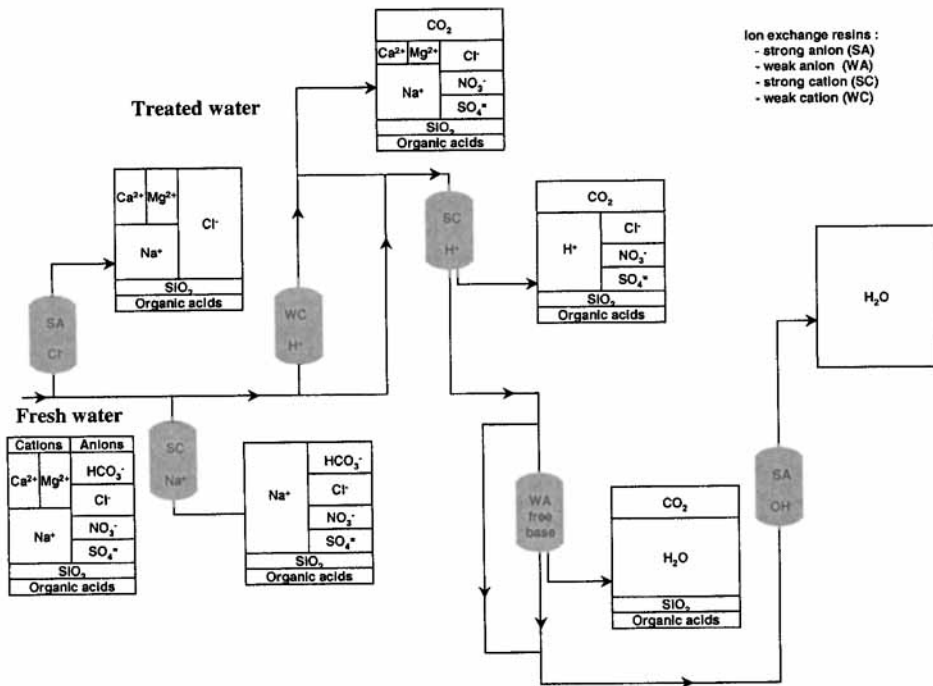


Diagram 1. The exchanges involved (F. Dardel, Techniques de l'Ingénieur, article J 2783).

fluid. This selective action can be used to separate certain phases, such as a suspension or a solute from the solvent. In the case of aqueous effluents, the principal membrane-based techniques are micro-filtration, ultra-filtration and nano-filtration, which employ porous membranes, together with reverse osmosis, which uses a dense pore-free membrane.

Porous membranes

When large volumes must be filtered, the process employed is 'tangential' filtration. The particles suspended in the liquid are entrained parallel to the membrane surface, preventing the latter from becoming obstructed. Only the very finest particles are able to traverse the membrane. Depending on the size of those retained, the process is termed micro-, ultra- or nano-filtration.

Reverse osmosis

This separation process is used to purify raw water by passing it through a semipermeable membrane under the influence of a pressure gradient. If two compartments are separated by a semipermeable membrane, with pure water on one side and raw water on the other, the pure water passes through the membrane until the chemical potentials are equal on both sides. The resulting difference in level corresponds to the osmotic pressure π . If now a pressure greater than π is exerted on the compartment containing the raw water, the flow is reversed, but only pure water is able to permeate the membrane, the salts being left to concentrate in the original compartment.

5.3.4. Iron and manganese removal

Iron and manganese are leached out from rock formations and are therefore found mainly in well waters. Since these waters generally have very low oxygen contents, these elements are always present as Fe^{2+} and Mn^{2+} ions. They combine with other chemical compounds to form inorganic and organic complexes.

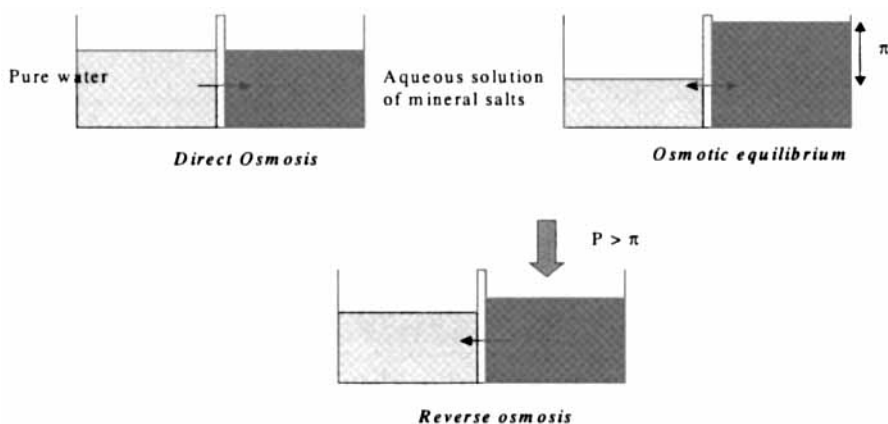


Fig. 5 Principle of reverse osmosis.

The iron and manganese initially present in a water can be eliminated by the formation of insoluble compounds, by oxidation to ferric and manganic hydroxides, or by conversion to ferrous and manganous carbonates or hydroxides in an alkaline medium.

5.3.4.1. *Oxidation processes.*

- By aeration/filtration for iron ($<10 \text{ mg L}^{-1}$), if the water does not contain manganese. At these concentration levels, the oxygen content of the water is sufficient.
- By 'oxidation' with oxygen, chlorine, chlorine dioxide, ozone or potassium permanganate. Manganese is more difficult to oxidise than iron, and chlorine dioxide, ozone and potassium permanganate give the fastest rates.
- By biological techniques. In an aerobic medium, numerous bacteria can be used to oxidise iron and manganese biologically. Oxidation is rapid and requires no additional reagent. The redox potentials are different ($>100 \text{ mV}$ for Fe and $>400 \text{ mV}$ for Mn), so that two treatment stages are required when both elements are present (biological filters).

5.3.4.2. *Precipitation associated with decarbonation.*

Decarbonation with lime generates a high pH, which promotes the elimination of iron and manganese in the form of carbonates and hydroxides.

6

Treatment of Water Circuits

Whatever the treatment of the feed-water, it is often necessary to add chemicals to the water in the cooling circuit. The products most commonly employed are:

- scale inhibitors and dispersants;
- corrosion inhibitors;
- biocides.

The choice of additives depends on the treatment philosophy adopted. Closed circuits necessitate specific conditioning. Once-through systems mainly require the use of microbiocides. They are wasteful of water resources and their replacement by recirculating water systems is encouraged.

6.1. Conditioning of closed circuits

So-called closed circuits are in fact slightly refreshed, since the ideal situation does not exist.

Water quality

Because of the relatively small losses, it is always economical to use high quality feed-waters.

Conditioning

Small volumes of feed-water enable the use of high inhibitor concentrations. Commercial formulations usually include several different inhibitors to ensure protection of all the metallic materials in the circuit. The most common inhibitors and formulations are described in Tables 8 and 9.

6.1.1. Product categories

6.1.2. Formulations

The different products are rarely used alone and are generally injected in the form of commercial mixtures known as 'formulations'.

Table 8. *Water treatment products for closed circuits*

Product	Role	Use	Advantages	Disadvantages
Borates	pH control	Used in combination with nitrites		
Chromates (not permitted in many parts of the world)	Anodic corrosion inhibitors	Used at high concentrations	High efficiency	Toxic to the environment Cannot be used in the presence of antifreeze (ethylene glycol) Risk of pitting if concentration too low.
Azole derivatives	Protection of copper	Low concentrations Complementary treatments	Highly protective films for copper and its alloys	
Hydrazine or substitutes (DEHA, etc.)	Oxygen reduction	Similar to boiler treatments. Applicable only to inert hot circuits.	Accelerates Fe_3O_4 formation Slightly increases pH	Decomposes to NH_3 at high temperatures. Risk of corrosion of copper
Molybdates (some environmental concerns)	Anodic corrosion inhibitors	pH>7 Presence of an oxidant necessary	High efficiency, low toxicity	High cost
Nitrites	Oxidising anodic corrosion inhibitors	pH 8 to 9 High concentrations	Good protection for iron- and tin-containing alloys	Needs the presence of a biocide. Oxidation of nitrites to nitrates Toxic to the environment
Phosphates	Anodic-Cathodic inhibitors	Used in combination with an oxygen reducer	Inhibition of corrosion	Increased calcium phosphate precipitation potential
Phosphonates	Inhibit precipitation of certain salts (iron phosphates)	Low concentration	Environmental compliance	Orthophosphate
Polyacrylates Polymers	Maintain suspended solids in suspension	Fouling/deposition		
Silicates		Protection of aluminium.	Environmental compliance	Problems when concentration too low
Sulphites	Oxygen reduction	Similar to boiler treatments Applicable only to inert hot circuits		

Table 9. Formulations for closed circuits

Nature	Comments
Base formulation	
Chromates	Not used in western world
Nitrites	Requires the presence of a biocide.
Nitrites + Molybdates	Requires the presence of a biocide.
Nitrites + Borates	Requires the presence of a biocide.
Molybdates + Phosphates	Requires $TH < 0.1 \text{ meq L}^{-1}$ and the presence of oxygen.
(Hydrazine or Sulphites) + Phosphates	Applicable only in an inert circuit.
Additional components	
Silicates	Used on a case-by-case basis with the above
Nitrates	formulations, depending on the water composition and
Azole derivatives	the specific features of the circuit.
Phosphonates	
Polyacrylates	

6.2. Treatment of Open Recirculating Water Systems

6.2.1. Treatment philosophies

6.2.1.1. Scale inhibition and/or dispersant treatments.

Stabilisation

In these treatments, additives are injected into the circuit to retard the precipitation of calcium carbonate, particularly at hot points. These products either increase the solubility limit or maintain the water in a state of super-saturation. They thus enable the circuit to operate at a higher concentration ratio. The major mechanisms involved are:

- sequestration/complexing, to form stable molecules with calcium and magnesium ions, and with certain other metal ions (iron, manganese, aluminium, etc.);
- poisoning of crystal nuclei;
- inhibition of crystal growth;
- a dispersion effect, involving adsorption onto crystal nuclei (e.g. alkaline earth salts), preventing aggregation or causing disintegration of already formed aggregates, maintaining the nucleating particles in suspension or in a state of dispersion close to their solubility limit.

Stabilisation treatments are very popular, since they allow operation at 'free pH'. The pH is then controlled by the CO_2 solubility equilibrium between the water

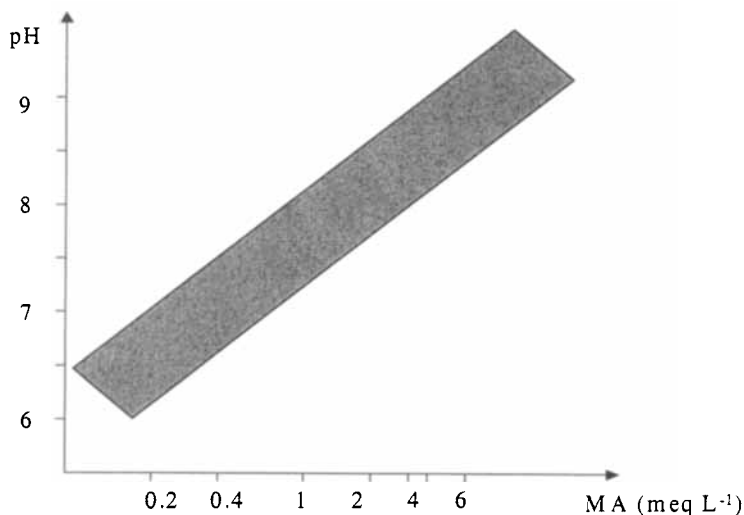


Fig. 6 Useful pH area of operation in cooling tower recirculation circuits ((90% of the experimental points fall in the hatched zone)

and the atmosphere, and becomes a simple function of the M-alkalinity level (MA).

Figure 6, established on the basis of experimental measurements in cooling tower recirculation circuits, indicates the usual fields of operation.

So-called 'free pH' treatments generally operate with a circulating water MA level between 3 and 9 meq L⁻¹, corresponding to pH values from 8.3 to 9.3 (the risk of corrosion is higher at lower pH values, while the risk of scaling is greater at higher MA levels). Monitoring of the pH value is therefore still necessary. Stabilisation processes using scaling inhibitors thus involve control of the formation of calcium carbonate deposits, which generally have a protective effect with regard to corrosion. The risks of corrosion are then limited by the slight scaling potential of the water and its high pH level.

However, although the efficiency of the scaling inhibitors and dispersants avoids excessive deposits, the protective calcium carbonate film can be sensitive to slight variations in the circuit parameters (acidity, lack of additives, etc.). In this respect, chlorides and sulphates accelerate the loss of protection and cause complications by increasing the conductivity of the water and hence the corrosion current.

pH control

The solubility limit of CaCO₃ is sensitive to the pH, which directly affects the concentration of carbonate ions. In order to prevent CaCO₃ precipitation, it is therefore possible to inject acid into the circuit to lower the pH. Sulphuric acid is usually chosen for this purpose. In fact, the addition of acid has two effects:

- it decreases the MA level by neutralizing HCO_3^- ions, forming CO_2 ;
- it lowers the pH if the CO_2 is generated more rapidly than it is removed from the circuit by degassing.

In this case, the quantity of acid necessary, expressed in g m^{-3} of feed-water, is determined from the formula

$$Q_{\text{acid}} = \frac{(\text{MA}_{\text{feedwater}} \cdot R_c - \text{MA}_{\text{max circuit}})}{R_c} k$$

If the sulphuric acid used has a concentration of 92%, then $k = 10.65$ (i.e. $100 \times 98 / 92 \times 2 \times 5$, where 98 is the molecular weight of the acid, 2 is the conversion factor to meq). The concentration ratio R_c must then be limited to maintain the conditions below the precipitation threshold for sulphates.

If hydrochloric acid is used, the limiting factor is the maximum chloride concentration permissible in the circuit.

In all cases, the water will become more corrosive, so that an additional treatment with corrosion inhibitors is generally necessary.

6.2.1.2. Corrosion inhibition treatments.

When corrosion protection is no longer ensured by the formation of calcium carbonate deposits, it is necessary to add a corrosion inhibitor to the circuit. These products form thin adsorbed films that do not hinder heat transfer. Most of them contain two active agents, in order to impede both the anodic and cathodic corrosion reactions. A minimum hardness and MA level (2 meq L^{-1}) is usually recommended to promote the formation of the protective layer.

Anodic inhibitors

These substances combine with the metal corrosion products, forming a completely insoluble salt, that is preferably adherent. If inhibition is purely anodic, large quantities of inhibitor are necessary (up to 1 g L^{-1} and more). This can only be envisaged in very small volume circuits, since any inhibitor deficiency can lead to accelerated localised attack.

Cathodic inhibitors

These substances combine with the products of the cathodic corrosion reaction, again forming insoluble compounds. Cathodic inhibitors involve lower risks than their anodic counterparts, since localised corrosion is not induced by a fall in their concentration, which merely causes a slight increase in the uniform rate, the latter remaining lower than in the complete absence of inhibitor.

Organic inhibitors

The effect of organic inhibitors is related to the formation of a continuous adsorbed film, which hinders electrochemical reactions at exposed surfaces. The film is formed by the physical or chemical adsorption of polar organic molecules

on the metal surface, so that the choice of molecules depends on the metal concerned.

Species that adsorb by physical mechanisms, involving electrostatic or Van der Waals forces, form films rapidly, but are easily removed, for example, when they are exposed to water without inhibitor.

Chemisorbed species, which form chemical bonds with the metal surface, create films that develop more slowly, but are more stable, due to their high adsorption energy. This is therefore the most favourable type for efficient inhibition. In particular, these compounds are used to protect copper and aluminium. Chemisorption depends on:

- the nature of the metal;
- the molecular structure of the inhibitor;
- the chemical nature of the bonding group;
- the inhibitor concentration.

Because organic inhibitors act by adsorption, they remain effective even in highly acid media ($\text{pH} < 4$), where corrosion depends on the H^+ ion concentration at the metal/water interface. At pH levels between 4 and 8.5, corrosion is generally controlled by the rate of oxygen diffusion at the metal/solution interface. In this case, the most efficient inhibitors are those that form a thick film, representing an effective barrier to oxygen diffusion from the solution to the metal. Finally, organic inhibitors can also operate in alkaline media, so that pH control is not necessary. However, pH control is used to reduce the scaling potential of the water and to allow the use of higher concentration ratios.

6.2.1.3. *Inhibition of growth of algae, bacteria and fungi.*

The choice of either a bactericide or a bacteriostatic formulation depends on the type of problem to be treated:

- in the presence of micro-organisms that induce biodegradation, such as SRBs, a bactericide should be used;
- in the presence of micro-organisms that act indirectly on corrosion phenomena, such as sludge-producing bacteria, the addition of a bacteriostatic reagent is to be preferred.

There are two major types of biocides:

Oxidising biocides

These substances destroy the micro-organisms by chemical oxidation. Their capacity to penetrate the cell walls and disturb the metabolism is an essential feature of their action, which is not selective, and in some cases depends on the pH.

Non-oxidising biocides

These species attack the micro-organisms by reacting with specific cellular constituents or by interfering with metabolic reactions. They either destroy the cell membrane or disrupt the 'biochemical machinery' involved in the production or use of energy. Their activity is selective and independent of pH. However, they are expensive and can cause waste problems, as several show little or no biodegradability. Their gradual destruction essentially involves chemical processes. For these reasons, ways are sought to reduce their consumption. These include transient shock treatments with larger doses, the use of reagents that adhere to the surfaces to be protected, and the use of blends of two or more biocides with synergistic interactions. When they are continuously used, bacteria develop resistance to such biocides. Many operators change their biocide every few weeks in order to prevent the development of biocide resistance in the bacterial populations.

6.2.2. Site-related constraints — selection guide

Before choosing a treatment philosophy (antiscaling reagent at free HCa, corrosion inhibitor at controlled pH, high or low R_c), it is necessary to identify all the pertinent circuit parameters. Once this has been done, the resulting constraints impose the major features of the treatment procedure. The information given in the tables below is not exhaustive and figures are given for guidance purposes only. Finally, the choice of treatment should not be based on a single criterion.

6.2.3. Product categories

Once the treatment philosophy has been decided, suitable formulations can be obtained from suppliers. The majority of these products are mixtures of different types of reagent, each chosen for a specific action. Tables 11 and 12 list the active substances found in these formulations, together with their role, their mode of implementation, and their advantages and disadvantages. The chemical formulae for some of these substances are given in Appendix D.

6.2.4. Formulations

Table 13 lists the principal formulations available today. They are liable to change with the increasing severity of environmental legislation and the development of new and improved products.

A classification has been established according to the different treatment philosophies outlined in § 6.2.1. Some of the formulations could be classified differently according to the relative contents of their components. The description of their make-up emphasises their specificity.

Note: The constituents of the formulations may be available either separately or in the form of a single commercial product.

In the majority of cases these formulations are not sufficient on their own and require additional treatments:

Table 10. *Selection guide*

Parameter	Constraints and selection data	Principal factors for the choice of treatment
Site		
Circuit distribution	• 1 circuit per unit • 1 circuit for several units, in series or parallel, with different ΔTs, flow rates and materials. • Circuits in cascade.	• Choose the treatment adapted to each circuit with an injection station per circuit. • Compromise overall treatment of the whole circuit allowing for the risk of contamination of each unit. • The treatments must be compatible from one circuit to another.
Storage of conditioning products	• A single storage point. • Several storage points.	• Requires a compromise involving a centralised overall treatment. • Possibility of decentralised treatments adapted to each circuit.
Management	• Simple • Complex	• Prefer an overall (compromise) treatment, either centralised or decentralised, depending on the storage points. • Possibility of defining a treatment adapted to each circuit with a (decentralised) post-injection for each of them.

Table 10. Selection guide (continued)

Parameter	Constraints and selection criteria	Principal factors for the choice of treatment
Circuit		
Materials	• Nickel alloys (B series) • Cu, Al • Stainless steels	• Require oxidant-free treatment, with limitation of the oxygen content. • Require special additional corrosion inhibition (azole). • Require adaptation of R_c depending on Cl^- concentration and the risk of deposits
Hot water temperature	• Avoid products unstable at temperatures above 60°C (polyphosphates).	• Add reagents to prevent precipitation in the water (dispersants, complexing agents, etc.).
Skin temperature	If very high (>90°C)(>60°C is considered hot in open recirculating cooling systems)	• Need to increase anti-scaling and dispersant treatments to avoid deposits. NB: some conditioning products can promote deposit formation.
ΔT	If too low	• R_c limited
Draining	If numerous uncontrolled and unrepairable leaks	• R_c limited • Allow for reagent losses and the risk of pollution.
Water flow velocity in heat exchangers	Depending on the material and the heat exchanger configuration: • If too high Cu >1 m s⁻¹ (higher for Cu-Ni alloys) Unalloyed steels >2 m s⁻¹ • If too low (<~0.5 m s⁻¹)	• Prefer corrosion inhibition treatments producing high stability protective films. • Pay particular attention to anti-scaling treatments, dispersants and biodispersants.
Slipstream filtration	None	• Need for feed-water with a low SS content. • Need to limit R_c • Appropriate dispersant treatment
Residence time (circuit volume and flow rate)	If high	• Need for a suitable biocide treatment • Beware of reagents involving biodegradable molecules.
Cooling tower materials	• Materials (wood and plastics) • Design (packing)	• Need for a suitable biocide treatment • Need for a suitable anti-scaling treatment

Table 10. *Selection guide (continued)*

Parameter	Constraints and selection criteria	Principal factors for the choice of treatment
Feed-water		
Quantity	Limited	• Advantage of increasing R_c to the maximum
Cost	High	• Advantage of increasing R_c to the maximum
Origin	Recycled or surface water	• Prefer a treatment that tolerates variations in water quality
Quality	• Fundamental parameters (pH, MA, TH) - If pH<6 • High salinity • Metal ions (Fe, Mn, Cu, Al) • Nutriments and microbiology • Suspended solids • Sulphur-containing compounds	• See Section 6.2.1 • Increase pH. Minimum pH should be 6.8 to 7.0 irrespective of treatment programme. Below 6.8 corrosion will increase markedly even with high levels of anodic inhibitors. • Need to limit R_c - Adapt the dispersants - Avoid alkaline media and modify the dispersants - Eliminate the source if concentrations high • Treat the feed-water with an oxidising biocide and modify the biocide treatment of the circuit. - Add specific dispersants - Adapt corrosion and deposit inhibition treatments - Verify the compatibility with organic compound additives • Reinforce the dispersant treatment and, if possible, the slip steam filtration • Pre-treat the water to avoid problems with copper and its alloys.

Table 10. *Selection guide (continued)*

Parameter	Constraints and selection criteria	Principal factors for the choice of treatment
Cooling water		
Malfunctions	Contamination (atmospheric pollution via towers, pollution via process, scaling, corrosion deposits, etc.)	Adapt the treatment to match the type of contamination (see Chapter 9: Malfunctions and remedial measures).
Draining		
Waste emissions	Towards: - The natural environment (respect regulations concerning certain parameters: AOX, metals, phosphorus, etc.) - Waste water purification station	- Choose an environmentally friendly treatment (beware of reagents liable to produce undesirable compounds in certain treatment conditions). - As for the natural environment. - Avoid products liable to perturb the operation of physico-chemical and biological purification processes (polymers, biocides).
Other uses of cooling water	Additional cooling or transfer to other circuits	Check the compatibility of the treatment with the conditioning used in the receiving circuit.

Table 11. *Scaling (S) and corrosion (C) inhibitors*

Active substance		Role	Use	Advantages	Disadvantages
Amines and fatty polyamines	C	Inhibition of corrosion by formation of a chemisorbed mono-molecular film on metal surfaces	• pH=7 to 9.5	• Excellent corrosion inhibition • Effective over a wide range of pH	• Low solubility in water → injection in the form of an emulsion. • need for a good surface condition.
	S	Scaling inhibitors that modify the crystal structure of CaCO ₃ (almost zero adherence of crystal nuclei).	• The anti-scaling effect can be enhanced by complexing agents or dispersants (phosphonates or polyacrylates)	• Prevent adhesion of sludges	
Azole derivatives	C	Corrosion inhibition (protection of copper)	• pH=7 to 9.5 • Low concentrations (1 to 3 ppm) • Used as additional treatments • Effects enhanced by certain amines (cyclohexylamine, alkanolamine, fatty polyamines).	• Formation of highly protective film on copper and its alloys. • Efficient over a wide pH range.	• Sensitive to oxidants, depending on the molecule. • High cost. • Odours possible in the case of chlorination.
Chromates (not used in Western World)	C	Anodic corrosion inhibitors	• Now forbidden in open and semi-once through systems.		
Molybdates (MoO ₄ ²⁻)	C	Anodic corrosion inhibitors	• pH>7 • Used in synergetic mixtures at concentrations of 5 to 20 ppm.	• Highly efficient.	• Risk of pitting if concentration too low. • High cost. • Require the presence of an oxidant.

Table 11. *Scaling (S) and corrosion (C) inhibitors (continued)*

Active substance		Role	Use	Advantages	Disadvantages
Ligno-sulphonates	C	Corrosion inhibition by differential aeration	• High concentrations (50–200 ppm) • Usually associated with polyphosphates	• Good resistance to oxidants. • Stabilise zinc in solution.	• Colour the water. • Additional biocide treatment (they provide large quantities of nutrient).
	S	Dispersants			
Tannins	C	Anodic corrosion inhibitors	• pH>8 • T>60°C		• Colour the water. • Need high chlorine contents — can lead to organic chloride contamination if Javel water[*] is used.
Phosphorus-containing organic compounds	S	Scaling inhibition by: - dispersion - impedance of crystal growth by adsorption on CaCO₃ nuclei.	• Concentrations often between 2 and 5 ppm. • Used with corrosion inhibitors. • Optimum pH range specific to each molecule.	• High efficiency. • Inhibit CaSO₄ • Stable up to 180–200°C.	• Do not control phosphate precipitation. • Molecules containing nitrogen are sensitive to strong oxidants. • Can accelerate attack of copper base alloys (case of ATMP). • Limited action for TH >12 meq L⁻¹. • Can hydrolyse to PO₄³⁻.
• Phosphonates, phosphonic acids • Phosphoalkyl-carboxylic acids					

*Javel water is an aqueous solution of sodium or potassium hypochlorite.

Table 11. *Scaling (S) and corrosion (C) inhibitors (continued)*

Active substance		Role	Use	Advantages	Disadvantages
Inorganic orthophosphates (PO_4^{3-})	C	Anodic corrosion inhibition if concentration >10 ppm, otherwise cathodic inhibitors.	• $\text{HCa} > 1 \text{ meq L}^{-1}$ (to promote protective layer formation). • Used in association with a dispersant. • Rarely used alone.	• High efficiency	• Sensitive to variations in pH. • Biocide recommended. • Presence of oxygen necessary.
‘Polycarboxylic’ acrylic polymers and copolymers • Polyacrylates • Polyacryl-amides • Polymeth-acrylates	S	Anionic dispersants. Retard and modify crystal formation.	• free pH • $\text{HCa} = 4 \text{ to } 10 \text{ meq L}^{-1}$ • $\text{TH} < 25 \text{ meq L}^{-1}$ • Generally associated with a phosphate or polyphosphate. • Used increasingly.	• Good stability at high temperature. • Good stability in the presence of chlorine. • Effective against precipitation of alkaline earth carbonates and sulphates	• Efficiency affected by flow rate.
Polyphosphates • Linear • Cyclic or polymeta-phosphates	C	Cathodic corrosion inhibitors	• Rarely used alone. • Need pH control.	• Compatible with chlorine treatments	• Partial inhibition of corrosion if employed alone. • Biocide recommended, since these substances are nutrients for bacteria.
	S	Scaling inhibition by: - dispersion - impedance of crystal growth by adsorption on CaCO_3 nuclei.	• Much less frequently employed.	• Improve protection. • Act on $\text{Mg}(\text{OH})_2$	• No effect on CaSO_4 precipitation. • Adsorbed by suspended clay particles or unfiltered flocks (to be used only in limpid waters). • Hydrolyse to PO_4^{3-} at temperatures $>60^\circ\text{C}$: → loss of scaling inhibition efficiency → formation of calcium salt scales. • Cyclic molecules hydrolyse less readily than linear ones.

Table 11. *Scaling (S) and corrosion (C) inhibitors (continued)*

Active substance	Role	Use	Advantages	Disadvantages
Silicates Silicate polymers	C Anodic corrosion inhibitors.	• Used preferably in soft waters.		• Risk of pitting at low concentrations. • Precipitate out with Ca and Mg.
Zinc: • Zinc salts • Organic zinc complexes	C Cathodic corrosion inhibitors.	The solubility of Zn at higher pH levels is increased by certain organic compounds (often associated with stabilisers to avoid precipitation).	• Good protection when there is a risk of localised corrosion. • No risk of localised corrosion at low inhibitor concentrations.	• Risk of zinc precipitation with sludge formation if: - high excess of Zn - pH too high (>8).
	S Scaling inhibitors	• Excess concentrations needed at the start of treatment, followed by maintenance at a low level (1 ppm to conserve the protective film). • Used in synergistic combination with other inhibitors.	• Can enhance the effect of certain biocides.	

Organic dispersants can also help to form uniform protective layers. Some more complex polymers, with carboxyl, hydroxyl, sulphonic or phosphorus-containing groups, have a more specific stabilising effect for alkaline earth carbonates, sulphates or phosphonates.

Table 12. Biocides and biodispersants

Active substance	Role	Use	Advantages	Disadvantages
Di- or trichloro-isocyanic acids	Oxidising biocides — react with the organic molecules in microbial cells (glucides and proteins).	Used with surfactants and biodispersants.	Prolong the presence of chlorine oxidising agent by stabilising the hypochlorous acid formed → improved sterilisation.	In the form of powder or granules difficult to use.
Quaternary ammonium salts	Non-oxidising cationic dispersants (hydrofuge surfaces and vectors for other biostatic bases).	Used as a routine treatment for 'trouble-free' circuits.	- Effective against algae and bacteria. - Cheap. - Efficiency impaired in the presence of heavy metals.	- Detergent effect that can cause foaming. - Cationic products incompatible with dispersants and sequestrants based on strong amines (high molecular weight polyacrylic derivatives, etc.).
Bromine and derivatives	Oxidising biocides — react with the organic molecules in microbial cells (glucides and proteins).	- Used alone or in combination with chlorine at pH>7.5. - Can be injected either in the feed-water or the circuit water.	- More powerful biocide than chlorine at basic pH levels and in ammoniacal media. - Generate less AOX than chlorine.	Same disadvantages as for chlorine (see below).

Table 12. Biocides and biocidal dispersants (continued)

Active substance	Role	Use	Advantages	Disadvantages
Chlorine or Javel water (Cl ₂ or HOCl)	Oxidising biocides — react with the organic molecules in microbial cells (glucides and proteins).	• Can be injected continuously or as a shock treatment in either the circuit or the feed-water. • Residual free chlorine is usually kept between 0.1 and 0.3 mg L⁻¹ (depending on national regulations) • Limited pH range (5 to 7.5)	• Cheap	• Non-selective action • Consumption of numerous organic and inorganic substances and reducing agents with an affinity for chlorine: - NH₃→chloramines - nitrites→nitrates - heavy metals (Fe, Mn) - certain polymers - H₂S→SO₄²⁻ • Difficult to maintain. • Problem of accessibility beneath deposits. • Ineffective against fungi, little effect on moulds. • Sensitive to light. • Sensitive to pH. • Enhances degradation of wood (certain streaming type cooling towers).
Chlorophenols	Non-oxidising biocides — attack cell membranes or block certain vital enzyme functions.	• No longer used (environmental toxicity).	• Highly efficient.	• Toxic towards the environment.

Table 12. Biocides and biodispersants (continued)

Active substance	Role	Use	Advantages	Disadvantages
Chlorine dioxide (ClO ₂)	Oxidising biocide — reacts with the organic molecules in microbial cells (glucides and proteins).	Used in circuits with pH range 6 to 10.	- Effective over a wide range of pH (6 to 10). - Does not react with NH₃. - Generates little AOX. - Very efficient (low residual of around 0.01 ppm).	- Must be produced on site near the circuit. - Needs a generator. - Possible problems depending on method of fabrication (corrosion, storage of products).
Guanidine derivatives with long aliphatic chains.	Non-oxidising biocides. Disperse mineral deposits (oxides)	Periodic injection at low concentrations.	- Excellent dispersal efficiency. - Effective at pH > 8. - Effective against algae, bacteria and fungi.	
Ozone (O ₃)	Oxidising biocide — reacts with the organic molecules in microbial cells (glucides and proteins).	Little used except in special cases.		- Must be produced on site. - Needs a generator. - Very sensitive to water chemistry (CaCO₃, HCO₃⁻, PO₄³⁻, etc.).
Methylene bithiocyanate (MBT) (C ₃ H ₂ N ₂ S ₂)	Non-oxidising biocide — attacks cell membranes or blocks certain vital enzyme functions.	- Periodic injection at low concentrations. - Generally used with a polyalkylene glycol type dispersant.	Effective against algae, sulphate reducing bacteria and fungi.	- Hydrolyses at pH >8 → reduced efficiency. - Low solubility in water. - Deactivated by Fe³⁺ ions.

Table 12. Biocides and biodispersants (continued)

Active substance	Role	Use	Advantages	Disadvantages
Isothiazolines	Non-oxidising biocides.	Act slowly (bacteriostatic reagents needing a long residence time).	• Wide range. • Do not foam. • Quite cheap. • Generate little AOX. • Effective in the presence of chlorine and bromine.	• Effective essentially against aerobic bacteria. • Low efficiency against algae. • Skin sensitiser which can lead to fairly serious reactions/allergies.
Glutaraldehyde	Non-oxidising biocide. Acts by deactivating or degrading proteins.	High concentrations (> 50 mg L ⁻¹).	• Can be analysed. • Non-foaming. • Efficiency increases with pH (up to 9). • Does not generate AOX. Effective in the presence of sulphides. Large range. Effective against SRBs.	• Efficiency reduced in the presence of ammonia (NH₃ > 10 mg L⁻¹). • Relatively expensive. • Withdrawn in UK due to HSE EH40 exposure limits
Enzymes	Hydrolyse biofilms.	• Very low concentrations. • Products under development. • Used in combination with biodispersants.	• Non-toxic, but effect on the environment unknown.	• Do not destroy bacteria. • Sensitive to pH, temperature, metals (Al, Fe, Zn), and ionic products.

Table 13. Formulations

Treatment philosophy	Formulations	Comments
Scaling <u>inhibition</u> and/or <u>dispersant</u>	Organic phosphorus / Molybdates Polymers Polymers / Lignosulphonates Polymers / Lignosulphonates / Zinc	Risk of precipitating zinc when pH too high (≈ 8) Need to control MA and maintain a minimum MA ($M > 3 \text{ meq L}^{-1}$)
By stabilisation — « free pH »	Polymers / Organic phosphorus Polymers / Organic phosphorus / Molybdates Polymers / Organic phosphorus / Zinc Polymers / Zinc	Use of an appropriate biocide (compatibility with polymer and quaternary ammonium — efficiency of the biocide as a function of pH).
By pH control	Organic phosphorus / Polymers / Orthophosphates Organic phosphorus / Polymers / Orthophosphates / Molybdates Organic phosphorus / Polymers / Polyphosphates / Zinc Organic phosphorus / Zinc	Phosphates used at medium and low concentrations ($< 8 \text{ mg L}^{-1}$)
<u>Anticorrosion</u> pH close to 7	Chromates / Zinc Chromates / polymer / Zinc Orthophosphate / Polymers / Organic phosphorus Orthophosphate / Polymers / Organic phosphorus / Polyphosphates Orthophosphate / Polymers / Organic phosphorus / Polyphosphates / Zinc Orthophosphate / Polymers / Organic phosphorus / Zinc Orthophosphate / Polymers / Zinc Orthophosphate / Organic phosphorus / Polyphosphate Orthophosphate / Organic phosphorus / Zinc Orthophosphate / Polyphosphate / Zinc Organic phosphorus / Polyphosphate / Zinc	Chromates are toxic towards the environment and are now forbidden for new treatments Phosphates used at medium and high concentrations ($8\text{--}14 \text{ mg L}^{-1}$) pH control Risk of Fe and/or Ca phosphate precipitation.

- azole derivatives for the protection of copper base alloys;
- appropriate biocides and biodispersants.

6.3. Selection Guide

Laboratory and/or on-site pilot tests

In order to gain a better understanding of cooling circuit problems, it may be necessary to perform tests in the laboratory or on a pilot installation in the field. For the results to be transposable to real circuits, it is necessary to:

- allow for the characteristics of the medium, performing tests in real plant water (e.g. when the water is recycled), with all the associated inspection procedures;
- simulate the major operating parameters of the real circuit, including the heat flux, the flow velocity, the presence of galvanic coupling, etc.

This approach has the advantage of taking into account the most important operating parameters. In this respect, an on-site pilot rig is intermediate between laboratory tests and field measurements. An installation of this type can be fed with a slip stream from the real circuit and equipped to measure most of the operating parameters.

Implementation of Treatment

Once the conditioning treatment has been defined, it is implemented in accordance with the specific features of the site. For closed circuits, the conditioning products are injected on startup. No further additions are necessary, except in the event of accidental draining or particular problems. In open recirculating water systems, the reagents, except for non-oxidising biocides, are injected 'continuously' with the aid of pumps in the feed reservoir. In some fairly rare cases, gravity injection is employed. Additional point treatments may sometimes be necessary in certain critical heat exchangers.

7.1. New Circuits

During circuit design, the possibility of complete draining must be allowed for. The need for chemical cleaning of the circuit before commissioning must be evaluated considering the state of cleanliness after installation.

7.2. Treated Circuits

7.2.1. Shutdown

Each circuit is unique and requires individual attention. Precleaning is sometimes performed during operation before shutdown, with the injection of complexing agents or dispersants to put deposited materials back into suspension, together with an increase in the drainage flow rate and a reduction in the concentration ratio. Two different situations can be distinguished:

- Total shutdown of the circuit with complete drainage, taking care to avoid corrosion problems associated with stagnant water. The reservoir is cleaned and the heat exchangers dismantled. New heat exchangers are given a special conditioning treatment. On system startup, rapid repassivation of the metal surfaces can be achieved by dosing the anodic inhibitor (usually phosphate) at up to three times the normal dosage rate.
- Total shutdown of the circuit without drainage. Only certain heat exchangers are dismantled and cleaned. On restarting, the prefilming treatment is not always applied. For circuits with poor quality feed-water (recycled waste waters), it is preferable, where possible, to restart with higher quality water.

7.2.2. Compatibility of treatments

If a change in supplier is envisaged, the same treatment philosophy should be maintained if it has been satisfactory. If it is decided to change the treatment

philosophy, care must be taken to ensure the compatibility of the different reagents employed. The concentration ratio in the circuit must then be reduced before applying the new treatment.

7.2.3. Modifications

If the circuit is extended, it is preferable to apply a prefilming treatment to the new part. The new operating conditions, including materials, residence time and flow velocity, must be considered to verify that the treatment products remain appropriate. If a heat exchanger is replaced, it is also recommended that the metal surfaces should be passivated rapidly by raising the anodic inhibitor levels for 2 to 3 days.

8

Monitoring and Inspection

8.1. Introduction

The reagents and equipment mentioned in this chapter are by no means exhaustive. The purpose is to describe existing plant and practices and not to advertise specific products.

8.2. Water Analyses

Feed-water compositions are monitored to check correct functioning of the circuit and to verify and control the injection of conditioning reagents.

Routine monitoring is rarely based on standard techniques (cf. Section 2.5.2) and tends to use colorimetric field methods, such as those of Hach, Lange, WTW, etc., with ready-to-use reagents and portable analysis equipment. The frequency of inspection depends on the quality of the feed-water and its variability, together with the critical nature of the circuit (residence time, reliability of conditioning reagent injection equipment) and the available online monitoring systems. For example, for a 'clean' feed-water of constant quality, it may be sufficient to monitor:

- pH
- TH and HCa
- salinity and/or conductivity
- metals (iron, copper, zinc, aluminium, manganese, etc.)
- chlorides.

For the circuit water, it is also necessary to check the concentrations of conditioning reagents (scale and corrosion inhibitors, oxidising biocide, etc.) and bacterial contamination levels (biological activity, SRBs, TRBs, etc.).

Examples of monitoring, depending on these parameters, are given in Section 11.

8.3. Methods for Evaluating and Measuring Corrosion

In order to ensure the durability of production equipment and the water circuits in general, it is necessary to evaluate:

- the rate at which the materials corrode, i.e. the loss in thickness;
- the nature of the corrosion, since localised attack is always more dangerous and insidious than uniform corrosion.

8.3.1. Gravimetric method

This method is based on the loss in weight of a test sample of the relevant material immersed in the circuit water. The measured weight loss is converted to an average thickness loss over the duration of exposure. The corrosion rate in mm/year is given by

$$V_{\text{corr}} = \Delta m.365 / (d.S.t \times 100)$$

where Δm is the weight loss in mg, t is the duration of exposure in days, S is the exposed surface area in cm^2 , and d is the density of the material in g cm^{-3} . In practice, field monitoring is performed by the exposure of test coupons, the material being as close as possible to that used in the circuit.

Coupon exposure

The coupon support systems vary depending on the circuit configuration. A number of conditions must be achieved:

- no galvanic coupling between samples or with the support material;
- positioning such that corrosion products from one coupon cannot induce corrosion on the others;
- continuous water flow over the surface of all coupons;
- avoidance of crevice formation;
- exposure of a surface area sufficiently large to enable accurate measurement of weight loss and examination of the surface;
- easy removal of specimens, particularly when a series of exposure times is planned;
- positioning in a critical zone (hot return water, rather than cold inlet water), at a sufficient distance from reagent injection points (particularly when the latter are acids or oxidising agents).

The exposure jig can be placed either in a diverted stream or directly in the circuit piping, with the aid of retractable rods, or even directly in the cooling water feed tank. The exposure time is usually 2 to 3 months, but durations of 1 year are useful to incorporate fluctuations due to variations in water quality, process conditions and treatments.

Weight loss measurements are complemented by visual and/or microscope examination to determine whether the corrosion is uniform or local. Observations are made directly after extracting the coupons, then after pickling, performed so as to remove deposits without damaging the metal substrate.

8.3.2. Electrochemical methods

Electrochemical methods are indirect and involve measurement of the polarisation resistance R_p , which is inversely proportional to the corrosion current i_{corr} (cf. Section 4.2.1). The measurement is performed with a probe comprising two, three, or even four electrodes. For field monitoring, the measurements of R_p are made with electrochemical sensors based on this principle. The probes must be placed in the water flow in such a way that the electrodes face into the current, with a water flow around each of them as nearly identical as possible. The apparatus makes measurements at regular intervals, enabling permanent monitoring of the corrosivity of the circuit water towards the materials placed in the probe. It is possible in this way to follow the corrosion of several different materials.

8.3.3. Advantages and disadvantages of these methods

Table 14 briefly summarises the advantages and disadvantages of the different techniques for measuring corrosion *in situ*.

Table 14. Advantages and disadvantages of corrosion measuring methods

Method	Advantages	Disadvantages
Weight loss	• possibility of large numbers of coupons • possibility of an applied stress, simulation of welds, crevices, etc. • ease of surface examination • possibility of analysing the surface and deposits	• long time for return of information — no alarm possible in the event of a rapid change in corrosivity • no information on the initiation and propagation of pits • in specimens exposed to a slip stream, no allowance for erosion or temperature gradients, etc.
Electrochemical probe	• rapid measurement • possibility of an alarm in the event of a rapid change in corrosivity	• risk of error in media with low conductivity • poorly adapted in the case of stainless steels • no information on certain types of corrosion (localised attack) • effects of temperature gradient, welds, etc. not considered

8.4. Methods for Evaluating Fouling and Scaling

Numerous direct and indirect methods exist for evaluating fouling and scaling, based on various proprietary systems.

8.4.1. Mineral fouling and scaling

Mineral and scale deposits can be monitored in two ways:

- in the circuit itself, by equipping the most sensitive or critical heat exchanger;
- on a loop parallel to the circuit, with or without instrumentation of specific heat exchangers.

Critical heat exchanger

The exchanger is generally chosen by the circuit operator, based on the severity of the working conditions to which it is subjected. At least one critical heat exchanger is designated per circuit. It is equipped on both the water and process fluid sides with a flowmeter and inlet and outlet temperature probes. The temperature and flow rate measurements at a given time enable calculation of the heat transfer coefficient, which reflects the degree of fouling of the exchanger. Monitoring of the variation of this coefficient with time (e.g. measurement once a day) provides information on the development of fouling.

Parallel loop

Parallel loops, generally installed by water treatment contractors, can be instrumented to varying degrees. In most cases, non-instrumented test exchangers are employed. Depending on the plant, these test exchangers may be heated by steam (with water flowing inside the tubes) or by electrical resistance heaters (with the water on the outside) — GE Betz or Ondeo Nalco type test exchangers. The flow rates and heat fluxes must be adjusted to operate in the most severe conditions encountered in the circuit evaluated (low water flow rate and high skin temperature). Fouling is monitored by dismantling the exchanger and weighing and examining the tubes. The maximum specified scaling rate is $50 \text{ g m}^{-2} \text{ y}^{-1}$.

For more detailed studies, or in more difficult circuits, instrumented mini-exchangers can be installed in the slip stream. In these systems, the water is made to flow in a channel at the surface of a wall heated electrically or by a hot fluid, with measurement of the temperature difference ΔT to determine the heat transfer resistance. These measurements are made under perfectly controlled operating conditions:

- In the steady state, either by monitoring ΔT in the exchange section for a stable heat flow (Seres Scalmatic and GE Betz Monitall techniques) or for a stable skin temperature (Bridger Scientific's DATS system used by Nalco). The ΔT value is used to calculate the heat transfer resistance.
- In the transient regime, the skin temperature being monitored on a surface previously subjected to a known heat flux, and compared to the values obtained on a reference surface (e.g. Rohrbach Scalometer).

Because heat transfer occurs, both of these approaches are well adapted to the monitoring of scaling. These techniques are also sensitive to biofouling, except for Scalmatic-type systems, which employ high flow rate automatic washing to eliminate fouling not characteristic of scale encrustment on the wall. Indeed, it is difficult to take into account only scaling phenomena and care must be taken in interpreting the results in terms of the risk of corrosion. The measurements are only relative, and absolute values are difficult to obtain. Furthermore, these systems give no information on the scaling potential of water with respect to polymer materials.

8.4.2. Biofouling

Biofouling is monitored essentially by means of visual observations, usually accompanied by bacteria counts. The observations are performed on metal or plastic coupons or glass balls, over which the circuit water flows at a slow velocity (GE Betz's Biobox and Biomonitor systems and Arcie's 'low velocity corrosion rack'). A wooden support may also be mounted in a plastic rig in which water flows at a low velocity (Nalco's Bioindicator).

Systems based on pressure drop measurement, such as that proposed by Ondeo Nalco, can also be employed to monitor biofouling. The water is made to flow through a calibrated tube, usually glass or stainless steel, and the pressure is measured at each end.

Biofouling can also be monitored by electrochemical methods, such as measurement of the free potential (a few mV) or the polarisation current. Few instruments based on this principle are available commercially in France, but some are marketed in other countries (Bigeorge probe and Atel Biofouling Monitor).

8.5. 'Automatic' Control of Treatment

Water treatment specialists propose numerous devices for the control of conditioning, from the simple control of pH to fully automated systems. Each operator must decide on the appropriate degree of automation depending on the circuit concerned:

- measurement of bleed and feed-water flow rates;
- measurement and control of pH;
- measurement of circuit water and feed-water conductivity (calculation of the concentration ratio);
- measurement and control of oxidant concentrations;
- analysis of conditioning reagent concentrations and circuit water parameters (turbidity, phosphate content, HCa, etc.);

- injection of conditioning products as a function of various criteria (bleed flow rate, tracer analysis, concentration ratio);
- stock management.

This monitoring can be performed remotely, with computer assistance and remote diagnostics.

NB: In the case of treatments at controlled pH, two pH meters must be available, one for control and one for monitoring and alarm purposes.

Malfunctions and Remedial Measures

The possible malfunctions are given in Table 15. The first column gives the parameters liable to warn of malfunctions when they vary outside of their usual

Table 15. Malfunctions

Parameter observed	Circuit parameter to be verified	Possible causes
Turbidity	- Suspended solids (SS) - Bacteria - Corrosion products - Consumption of conditioning reagents	- Functioning of diverted filter - Feed-water contamination by SS - Process leaks - Conditioning reagents (nature and/or concentration)
Foam		- Conditioning products (biodispersant, etc.) - Process leaks
Online monitoring	For online monitoring, first of all, check the consistency of the measurements in the laboratory and review them.	
pH	- Laboratory pH - Reagent consumption under pH control	- Nature and quantity of conditioning reagents - Process leaks - Feed-water (flow rate and quality) - Bleed flow rate - Atmospheric pollution
Conductivity	- Laboratory conductivity - Hardness (TH) - HCa R_c	- Bleed and feed-water flow rates - Feed-water quality or contamination - Process leaks - Nature and quantity of conditioning reagents - Atmospheric pollution - Scaling
Conditioning reagents and oxidants	Laboratory analysis of the nature and concentration of conditioning reagents	- Valve servocontrol system - Product conformity - Process leaks - Feed-water contamination - Reagent degradation due to circuit conditions (pH) - Defective feed (ice, leaks)

Table 15. Continued

Parameter observed	Circuit parameter to be verified	Possible causes
Critical heat exchanger temperature	• Process fluid and/or water flow rates • Water quality	1) Modification of the operating conditions 2) Scaling and/or fouling
V_{corr}	• Verify probe	1) Process modification 2) Nature and quantity of conditioning reagents and oxidant 3) Process leaks 4) Feed-water quality or contamination 5) Atmospheric pollution

Table 16. Remedial actions

Cause	Actions
Loss of efficiency of the slip stream filter	• Check the filter input • increase the washing frequency • Check the efficiency of cleaning (measure SS in the washing water) • Apply an appropriate treatment (Javel water, air, specific reagent, etc.) • Change the support material
Pollution or variation of feed-water quality	
• SS, corrosion products, metals, pH	• Check the efficiency of the raw water treatment (if filter, idem above) • Adapt the treatment and the R_c • Treat the feed-water and adapt the R_c
• Bacteria	• Adapt the treatment and identify the origin of the leak (isolate it if possible) • Analyse the type of corrosion responsible for the leak • Change of material if the process allows it
Process leaks	
Conditioning reagents	
• Servocontrol valves or feed defect • Product conformity • Reagent degradation due to circuit operating conditions	• Repair the injection circuits • Restore the initial formulation • Choose a treatment insensitive to these conditions
Bleed or feed-water flow rate	• Restore the proper operating conditions
Atmospheric pollution	• Adapt the treatment
Scaling and fouling	• Clean the circuit • Adapt the treatment • Consider the installation of a diverted filter
Modification of the operating conditions	• Adapt the treatment

range. The second column indicates the principal circuit parameters to be measured and compared with the corresponding set values. The third column lists the major possible causes in the order of decreasing probability.

For the principal causes of malfunction given in column 3 of Table 15, Table 16 indicates a number of possible remedial actions.

10

Legal Aspects

When defining a treatment for cooling water circuits, the aim is first of all to minimise corrosion, scaling and mineral and biological fouling. Apart from their intrinsic properties, the reagents used to ensure satisfactory plant operation must meet increasingly severe environmental constraints. Such environmental considerations have led to the disappearance of certain conventional inhibitors such as chromates and zinc, together with a number of synthetic biocides and bactericides.

In the case of cooling circuits, one of the most important points is the eventual elimination of all once-through systems, except by special permission, in order to reduce water consumption. For certain industries (e.g. oil refining and petrochemicals), the decree defines the maximum quantities of water not to be exceeded. Specifications regarding waste emissions include limitations in terms of COD, BOD 5, TOC, SS, oxidised and reduced nitrogen, phosphorus and pH ('principal parameters'), together with constraints concerning:

- waste emission temperatures;
- phenol index;
- phenols;
- hexavalent chromium;
- cyanides;
- arsenic and its compounds;
- lead and its compounds;
- chromium and its compounds;
- nickel and its compounds;
- zinc and its compounds;
- manganese and its compounds;
- tin and its compounds;
- iron and aluminium and their compounds;

- adsorbable organically bound halogens (AOXs);
- total hydrocarbons;
- fluorine and its compounds.

In addition to these substances, the so-called micro-contaminants listed in the EEC directive 76/464 must also be controlled. Among all these species, zinc and phosphates are important constituents of many corrosion inhibitors, while AOXs and chlorophenols can be generated by chlorination of a cooling circuit.

Thus, when defining a circuit treatment, care must be taken to ensure that it does not give rise to wastes liable to create problems with regard to the permissible overall plant emission levels.

11

Examples of Treatments and Monitoring

Table 17 gives examples of treatments used in different types of industrial plant. The cooling circuits and the qualities of the feed and circuit waters are described, together with the treatments currently employed. The choice of plants has been made to cover a wide range of conditioning treatments. A few comments on the choice of treatment and possible alternatives are given at the end of the chapter.

Table 17. *Examples of treatments and monitoring*

Plant type	1) Refinery.	2) Petrochemicals.	3) Polymers.	4) Fertilisers.
	Several independent circuits with direct discharge to the waste water treatment plant.	Several independent circuits with direct discharge to the waste water treatment plant.	One circuit with direct discharge to the waste water treatment plant.	Several circuits with waste disposal by deep injection.
	Common treatment for all circuits.	One treatment per circuit		Common treatment for all circuits.
Constraints	No acid control and limited zinc emissions.	Heavy metal emissions limited.	No acid control and no zinc emissions.	Limited chloride emissions.
Circuit				
Number of exchangers	66	9		32
Materials	Water inside tubes. Steel, brass.	Water inside tubes. Steel	Water outside tubes. Steel, stainless steel.	Water inside tubes. Steel, stainless steel, brass, titanium.
Cooling tower	Forced draught	Forced draught	Forced draught	Forced draught
Volume (m ³)	4200		200	1530
Flow rate (m ³ h ⁻¹)	6900	3200	550	5200
Diverted filtration (m ³ h ⁻¹)	Parallel filters (2 × 80)	150	50 (incl. feed-water)	80
Feed-water flow rate (m ³ h ⁻¹)	160	30	5	70
Bleed flow rate (m ³ h ⁻¹)	80	5	2	20
Max. skin temp. (°C)	100	100	80	
ΔT (°C)	10		6	5

Table 17. Examples of treatments and monitoring (continued)

Feed-water					
Origin	Surface water	Surface water	Well water	20% well water–80% recycled water.	
Pretreatment	Chlorination and sand filtration	Flocculation–coagulation, sand filtration and chlorination	Sand filtration	Chlorination and sand filtration for recycled water.	
				Well	Recycled
Quality: pH	7.5–8	7.6–7.8	6.4–6.8	7–7.5	8.3
MA (meq L ⁻¹)	4.4	2.8–3.2	1–2.4	5	27
TH (meq L ⁻¹)	6	3–4	2.4–4.2	7.2	5
Conductivity (µS cm ⁻¹)	580	390			2400
Chlorides (mg L ⁻¹)	40	20–35	16–30	35–40	35
SS (mg L ⁻¹)	3	<5			1
Fe (mg L ⁻¹)	0.06	0.05	0.5	0.12	
Si (mg L ⁻¹)	9			9	2.5
Phosphates (mg L ⁻¹)	0.5			30–40	20
Sulphates (mg L ⁻¹)	32			500	
Ammonium (mg L ⁻¹)				35	
Nitrates (mg L ⁻¹)					
Conditioning					
Scaling/corrosion inhibitors	Sulphonated carboxylic polymers Glycol esters Exceptionally Zn	Inorganic phosphate Polymers Organophosphates	Inorganic phosphate Molybdate Organophosphates	Organophosphates Acrylic polymers	
Biocide/biodispersant	Javel water + bromine Organosulphides + polyaldehyde	Javel water + biocide + synthetic biodispersant	Javel water + bromine + biodispersant	Chlorine dioxide	
Concentration ratio	1.8	5.5–6.5	4	3.5–3.9	
Settings	Circuit HCa = 8 meq L ⁻¹ ± 0.6	pH = 7 ± 2 TH max = 25 meq L ⁻¹		Chlorides > 300 mg L ⁻¹	

Table 17. Examples of treatments and monitoring (continued)

Circuit water				
pH	Free	6.8–7.2	8.3–8.6	8–8.2
MA (meq L ⁻¹)	8	0.55	2.8–5	8
TH (meq L ⁻¹)	10	22	9–14	13
Conductivity (μS cm ⁻¹)		2000	1000–1500	2600–3000
Chlorides (ppm)	82		70–140	200–300
SS (ppm)	4			8–15
Fe (ppm)	0.05	0.9	0.7–2.8	0.2
Si (ppm)				10
Phosphates (ppm)		13	12	6.5
Sulphates (ppm)				76
Free C _{l2} (ppm)	0.2	0.3		
Monitoring				
On-line instrumentation	None	pH control Continuous monitoring of free chlorine		pH control Control of inhibitor
Corrosion monitoring	Corrosion rack with coupons and probe in return hot water. Coupons in critical heat exchangers.	Corrosion racks with coupons	Corrosion rack with coupons in return hot water.	Corrosion rack with coupons in return hot water. Coupons in critical heat exchangers.
Scaling monitoring	Heat transfer coefficient in critical heat exchangers. Test exchanger.	Heat transfer coefficient in critical heat exchangers. Test exchanger.		
Biofouling monitoring	Bacteria count. Low velocity rack with coupons in return hot water.	Bacteria count.	Bacteria count. Detection of SRBs in circulation and beneath deposits.	Bacteria count (‘biodetector’).

Table 17. *Examples of treatments and monitoring (continued)*

Results and problems encountered	Corrosion rate $80 \mu\text{m y}^{-1}$ Corrosion peaks during hydrocarbon leaks, with proliferation of bacteria.	Corrosion rate $< 25 \mu\text{m y}^{-1}$ on coupons exposed 90 days. Corrosion peaks during malfunction of the pH control.	Corrosion rate $20 \mu\text{m y}^{-1}$ on coupons exposed 12 months.	Corrosion rate $20 \mu\text{m y}^{-1}$. Corrosion peaks during process acid leak.
	Scaling correctly controlled. Presence of a film of bacteria and algae in the hot water tank. Proliferation of bacteria during warm seasons and during hydrocarbon leaks. Variable feed-water quality.	Scaling correctly controlled. Difficulty in maintaining an optimum concentration ratio due to accidental draining.	Scaling correctly controlled. Marked fluctuations in feed-water quality.	Scaling correctly controlled. Marked seasonal proliferations of bacteria. Variation in the quantity of feed-water depending on workshop activity and rainfall.

Comments

- In order to apply the treatment used in example 1 to example 2, the maximum concentration ratio would be 4, and this is incompatible with the local site constraints.
- For example 3, treatment 2 could be used provided that pH control is adopted.
- For example 4, any treatment envisaged is subject to prior testing, since the effect of this water quality is prejudicial to the efficiency of the formulations currently in general use.

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Appendix A

Calcium/Carbonic Species Equilibria and Carbonate Deposits

General principle

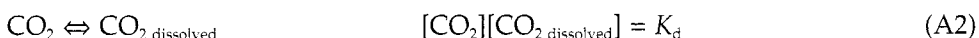
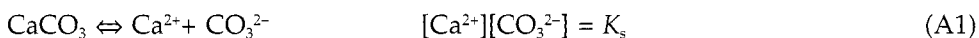
The carbonate deposits produced during scaling involve different forms of calcium carbonate (calcite, aragonite, vaterite), and only exceptionally magnesium carbonate (dolomite). For the sake of simplicity the following discussion will consider only CaCO_3 .

Water contains numerous species in solution, most of which have no direct influence on CaCO_3 precipitation. Indeed, the latter depends only on the pH, the principal parameter on which water treatments are based, and naturally, on the concentration of Ca^{2+} ions and carbonic species. In order to simplify the approach, a distinction will be made between:

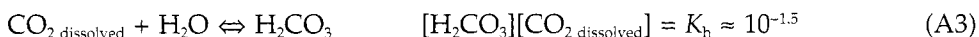
- the so-called ‘characteristic’ ions, whose concentrations are invariable, since they take part in none of the equilibria involved in CaCO_3 precipitation: Na^+ , K^+ , Mg^{2+} , Cl^- , SO_4^{2-} etc.; and
- the ‘fundamental’ ions involved in these equilibria: Ca^{2+} , H^+ , OH^- , HCO_3^- , and CO_3^{2-} .

These equilibria represent either solubility (CO_2 , CaCO_3), hydration (H_2CO_3), or dissociation (water, carbonic species). Each equilibrium is governed by its mass action law.

Solubility equilibria



Hydration equilibria

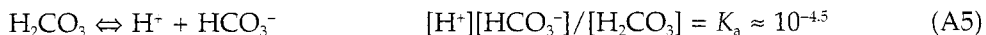


Dissociation equilibria

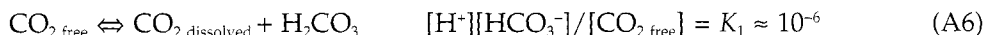
Water



First dissociation of carbonic acid



Since the value determined analytically is the total CO_2 , (A3) and (A5) are combined to give:



where

$$K_1 = K_a K_h (1 + K_h) - 1 \approx K_a K_h \quad (\text{A7})$$

Second dissociation of carbonic acid



In order to simplify the discussion, **all concentrations are expressed in eq L⁻¹**. It should also be noted that all the equilibrium 'constants' in fact vary with both temperature and the ionic potential of the solutions. The ionic potential μ is given by:

$$\mu = 0.5 \sum m_i z_i^2 \quad (\text{A9})$$

where m_i is the concentration of species i in mole L⁻¹ and z_i is the valency of the ionic species i . It has been seen that the concentration of H^+ ions is present in several of the above equilibria, and it is therefore not surprising that the evaluation of the state of saturation of a water with respect to CaCO_3 involves comparison of the measured pH level with different calculated values.

Examples of the calculation of the pH of a water

The basic equation for calculating the pH is that for electrical neutrality, expressing the fact that the sum of the concentrations of all the ions in solution represents the overall stoichiometry of the different dissolved salts:

$$[\text{H}^+] + ([\text{Ca}^{2+}]) + \Sigma C_i = [\text{OH}^-] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] + \Sigma A_i \quad (\text{A10})$$

where ΣC_i and ΣA_i are, respectively, the sums of the characteristic cation and anion concentrations. Depending on whether or not $[\text{Ca}^{2+}]$ is variable (solubility equilibrium) or invariable (water either under saturated or metastably supersaturated), $[\text{Ca}^{2+}]$ will be either considered separately or included in ΣC_i .

Using Poirier's notation, the difference between the concentrations of characteristic anions and cations is defined as the parameter λ :

$$\lambda = \Sigma A_i - \Sigma C_i \quad (\text{A11})$$

The value of λ is a constant. It is calculated from equation (A10) by reference to the water analysis conditions. It is thus expressed differently according to whether $[\text{Ca}^{2+}]$ is considered as variable or constant, and therefore may or may not be incorporated in λ . In an unsaturated water ($[\text{Ca}^{2+}]$ not incorporated), λ is then the 'alkalinity' of the water, i.e. the sum of the concentrations of OH^- , HCO_3^- and CO_3^{2-} ions under the conditions of the analysis. The pH is calculated by replacing the terms of equation (A10) in equations (A1) to (A8).

Water undersaturated with respect to CaCO_3 or metastably supersaturated

$[\text{Ca}^{2+}]$ is constant, so that

$$[\text{H}^+] - \lambda - [\text{H}^+]^{-1}(K_w + K_1[\text{CO}_2 \text{ free}](1 + K_2[\text{H}^+]^{-1})) = 0 \quad (\text{A12})$$

Water saturated with CaCO_3

$[\text{Ca}^{2+}]$ is variable, so that:

$$[\text{H}^+]K_s(K_1K_2[\text{CO}_2 \text{ free}])^{-1} + [\text{H}^+] - \lambda - [\text{H}^+]^{-1}(K_w + K_1[\text{CO}_2 \text{ free}](1 + K_2[\text{H}^+]^{-1})) = 0 \quad (\text{A13})$$

These equations can only be solved either numerically or approximately. For example, as soon as the free CO_2 concentration exceeds $10^{-4} \text{ meq L}^{-1}$ ($1 \mu\text{g L}^{-1}$), the term K_w becomes negligible ($[\text{OH}^-] \ll [\text{HCO}_3^-]$). This enables equations (A12) and (A13) to be simplified:

Water undersaturated with respect to CaCO_3 or metastably supersaturated

$$[\text{H}^+] - \lambda - K_1[\text{CO}_2 \text{ free}][\text{H}^+]^{-1}(1 + K_2[\text{H}^+]^{-1}) = 0 \quad (\text{A14})$$

Water saturated in CaCO_3

$$K_s(K_1K_2[\text{CO}_2 \text{ free}])^{-1} + [\text{H}^+]^2 + [\text{H}^+] - \lambda - K_1[\text{CO}_2 \text{ free}][\text{H}^+]^{-1}(1 + K_2[\text{H}^+]^{-1}) = 0 \quad (\text{A15})$$

Similarly, in acidic or neutral waters ($\text{pH} < 8$), the last term in these equations is negligible (carbonate $\ll$ bicarbonate). This leads to simple asymptotic laws of the type:

Alkalinity-free water

$$\text{pH} = 1/2 pK_1 - 1/2 \log[\text{CO}_2 \text{ free}] \quad (\text{A16})$$

Acidic or neutral water undersaturated with respect to CaCO_3 or metastably supersaturated

$$\text{pH} = pK_1 + \log[\text{HCO}_3^-] - \log[\text{CO}_2 \text{ free}] \quad (\text{A17})$$

Acidic or neutral water saturated in CaCO_3

$$\text{If } [\text{Ca}^{2+}] \approx [\text{HCO}_3^-]: \text{pH} = 1/3(2pK_1 + pK_2 - pK_s) - 2/3\log[\text{CO}_2 \text{ free}] \quad (\text{A18})$$

$$\text{If } [\text{Ca}^{2+}] \gg [\text{HCO}_3^-]: \text{pH} = 1/2(pK_1 + pK_2 - pK_s) - \log[\text{Ca}^{2+}] - 1/2 \log[\text{CO}_2 \text{ free}] \quad (\text{A19})$$

$$\text{If } [\text{Ca}^{2+}] \ll [\text{HCO}_3^-]: \text{pH} = pK_1 + \log[\text{HCO}_3^-] - \log[\text{CO}_2 \text{ free}] \quad (\text{A20})$$

Saturation index

Following the example of Langelier, several indices have been successively proposed to characterise the degree of saturation of a water (Legrand-Poirier, Stiff and Davis). In fact, they all finally evaluate the same physical parameter, that is the degree of saturation in CaCO_3 . This is defined by the ratio between the effective solubility product of CaCO_3 and its equilibrium value K_s :

$$(\text{CaCO}_3)_{\text{sat}} = [\text{Ca}^{2+}][\text{CO}_3^{2-}]/K_s = [\text{Ca}^{2+}][\text{HCO}_3^-]/[\text{H}^+]K_s \quad (\text{A21})$$

By definition, a saturated water thus has a degree of saturation equal to 1. Using equations (A1) to (A8), the parameter pH_s is then defined as the pH of a water of the same ionic composition assuming that it is in calcium:carbonic species equilibrium:

$$[\text{Ca}^{2+}][\text{CO}_3^{2-}] = [\text{Ca}^{2+}][\text{HCO}_3^-] K_2/[\text{H}^+]_s = K_s \quad (\text{A22})$$

whence

$$\text{pH}_s = pK_2 - pK_s - \log[\text{Ca}^{2+}] - \log[\text{HCO}_3^-] \quad (\text{A23})$$

Comparison of (A21) and (A23) shows that the difference between pH_s and the measured pH value, pH_0 , (Langelier index I_L) is precisely the degree of saturation of the water in CaCO_3 :

$$I_L = \text{pH}_0 - \text{pH}_s = \log (\text{CaCO}_3)_{\text{sat}} \quad \text{or} \quad (\text{CaCO}_3) = 10^{I_L} \quad (\text{A24})$$

This gives the key to the meaning of the Langelier index:

If $I_L = 0$ the water is saturated and just at equilibrium

If $I_L < 0$ the water is undersaturated and therefore aggressive towards marble

If $I_L > 0$ the water is supersaturated and therefore potentially scaling.

It should be noted that the Langelier index is not sensitive to the units of measurement provided that they are homogeneous (moles or equivalents per litre).

Stability index

The effective precipitation of CaCO_3 naturally requires sufficient supersaturation, which is unfortunately quite variable, depending in particular on the temperature. Various empirical stability indices have therefore been proposed, the most reliable being that of Ryznar:

$$I_R = 2pH_s - pH_0 = pH_s - I_L \quad (A25)$$

This index empirically combines the degree of saturation I_L with the ionic concentrations, via equation (A23).

Ryznar scale	
I_R	Water behaviour
4.5 to 5	Highly scaling
5 to 6	Weakly scaling
6 to 7	Weakly corrosive
7 to 7.5	Corrosive
7.5 to 9	Highly corrosive
> 9	Very highly corrosive

Practical application

The difficulty in applying these indices was for a long time the problem of the exact value of pH_s to insert in the Langelier index. Nevertheless, the thermodynamic calculations involved in the Legrand-Poirier method are now easy to perform with the aid of computers.

Appendix B

Scaling Mechanisms

This appendix is naturally limited to the precipitation of CaCO_3 in cooling water circuits.

The different modes of precipitation of calcium carbonate

It has been noted in Appendix A that precipitation is only possible when the water is supersaturated in CaCO_3 , i.e. when the degree of supersaturation δ is greater than 1. If this is not the case, then the only possibility is dissolution of any solid carbonate already present:

- $\delta < 1$: the water is undersaturated and potentially aggressive towards marble;
- $\delta = 1$: the water is in equilibrium, and no reaction can occur;
- $\delta > 1$: the water is supersaturated and CaCO_3 can precipitate.

However, these criteria consider only the bulk thermodynamic requirements and neglect kinetic aspects. Like all precipitation reactions, the process involves nucleation and growth. This means that for stable CaCO_3 particles to appear within the liquid phase, 'nuclei' of a certain critical size, capable of subsequent spontaneous growth, must first of all be formed. The elementary process of nucleus formation involves the association of hydrated CO_3^{2-} and Ca^{2+} ions to produce pairs, which group together to give an electrically charged colloidal embryo, characterised by its potential ζ . When this embryo or nucleus exceeds the critical size, it can grow by the addition of further ion pairs, tending to become dehydrated in the process, leading to a well-formed crystal. The crystal itself then continues to grow.

Both nucleation and growth depend directly on the degree of supersaturation δ . Because of nucleation constraints, the condition $\delta > 1$ is not sufficient for precipitation to occur and experience shows that a value of δ of the order of 40 is necessary for massive precipitation at ambient temperature. This is reflected in the stability indices, such as that due to Ryznar. However, it is preferable to use a computer-assisted version of the Legrand-Poirier method to monitor variations in δ , based on analyses at different points in the circuit.

Beyond this threshold δ value, precipitation in clear water is almost certain. This is the domain of 'homogeneous' precipitation. For δ levels between 1 and 40, 'heterogeneous' precipitation can occur at specific nucleation sites, the probability increasing as the value approaches 40. Clear water with $\delta > 40$ is thus fully unstable, while when $1 < \delta < 40$ it is simply metastable. The deliberate addition or accidental presence of certain substances can facilitate nucleation and increase the probability of precipitation for δ values between 1 and 40, while others can have the opposite effect, inhibiting nucleation.

Even when a water is able to form CaCO_3 nuclei, it will not necessarily cause scaling, and can therefore best be described as being 'calcifying'. In fact, the CaCO_3 nuclei can evolve in different ways:

1. The nucleus begins to grow, then moves to another region where the water composition is such that it redissolves.
2. The nucleus formed in the liquid grows into a crystal and settles out as a sludge.
3. The nucleus forms on a metal wall, and provided that the adhesion forces are sufficiently strong, scaling occurs.
4. The nucleus is trapped by a non-conducting wall, and will again cause scaling if the adhesion forces are sufficiently strong.
5. The nucleus remains suspended in the water and is entrained by the flow.

It is thus important to know the local values of δ at all points in the circuit. If δ is sufficiently high throughout the volume of water, precipitation or nucleation will be global. Conversely, if a high δ value is attained only in certain regions, then nucleation and precipitation will be local. Nevertheless, the nuclei formed can be disseminated throughout the circuit, where they can have various effects.

Scaling

1 – *Interaction between CaCO_3 nuclei and circuit walls.* When a water is ‘calcifying’ and does not contain excessive amounts of impurities and suspended solids, the calcium carbonate nuclei are colloidal particles with a positive electric charge (positive potential ζ). Like all interfaces between two phases, the cooling circuit walls are also electrically charged, leading to an electrostatic interaction with the CaCO_3 nuclei. If a positively charged nucleus is entrained in the vicinity of a **metallic** wall, which is usually negatively charged (e.g. corroding steel), it will be attracted onto the surface. Two situations are then possible:

- The nucleus is adsorbed and strongly adheres to the wall, initiating scaling. It should be noted that nuclei can be created directly on such walls as a result of local electrochemical reactions, particularly corrosion.
- The nucleus forms within the liquid, probably growing to a larger size than in the previous case, and is simply attracted to the metal surface, without being really adsorbed. The adhesion is therefore weak. In this case, it can act as a local growth point by trapping excess CO_3^{2-} and Ca^{2+} ions. It will therefore prevent the formation of new nuclei on the wall, thus acting as a scaling inhibitor.

If the surface corrodes, certain ions are emitted in the anodic zones and are subsequently dispersed in the water, where they may either catalyse nucleation (e.g. Fe^{2+} ions) or act as inhibitors (e.g. Cu^{2+} , Zn^{2+} and Pb^{2+}).

In the case of certain **insulating** (non-metallic) surfaces, the phenomena are similar, even though the nature of the surfaces leads to a different type of adhesion. For glass surfaces, local alkalinity can be high and nucleation can occur

directly on the wall, leading to strongly adherent scale formation analogous to that for metallic surfaces. Like metal walls, weak, purely electrostatic adhesion of nuclei previously formed in the liquid can also occur in this case.

In contrast, for polymer walls, the only possible attractive forces are electrostatic in nature, since most polymers remain chemically neutral with regard to the formation of CaCO_3 . Indeed, it has been demonstrated that scaling on polymer surfaces is due to a purely electrostatic mechanism. Since the CaCO_3 nuclei present in the water are positively charged, they are attracted by the insulating walls, which become negatively charged in the water. The CaCO_3 nuclei can therefore be readily adsorbed. It has been shown that it is the smallest nuclei, formed in the initial stages of precipitation, that are most easily trapped on polymer surfaces.

2 – *Deposit growth on walls.* In the case of both metallic walls and polymer-based insulating walls, the first nuclei adsorbed can serve as growth sites for excess CaCO_3 . However, once the wall is completely covered, subsequent growth is independent of the type of substrate material. The interface with the water then becomes a surface of calcium carbonate that behaves as an insulating barrier. It can both act as a growth site (general situation in clear waters) and continue to electrostatically trap sufficiently fine CaCO_3 nuclei in the water. Deposit build-up can thus occur by these two different mechanisms.

General characteristics of scaling observed in cooling circuits

Cooling circuits generally include various materials. The heat exchangers mainly involve metals and alloys, while cooling towers usually contain numerous plastic transfer surfaces. All the mechanisms described above can often occur simultaneously and the calcium carbonate can have several forms:

- colloidal nuclei that remain in solution due to their electrical charges;
- nuclei that have coarsened to crystallites, liable to settle out in zones of low turbulence, forming sludges;
- adherent scale on walls.

When the degree of supersaturation is high, either locally or throughout the circuit, the resulting nucleation can either cause scaling or have an inhibiting effect, depending on the nature of the walls. It is the nucleus growth kinetics that are the important factor. If the nuclei grow rapidly, they will have an inhibiting effect. If they remain small, in an electrically charged colloidal form, the risk of scaling is high, particularly on insulating surfaces.

Appendix C

Ion Exchange Processes

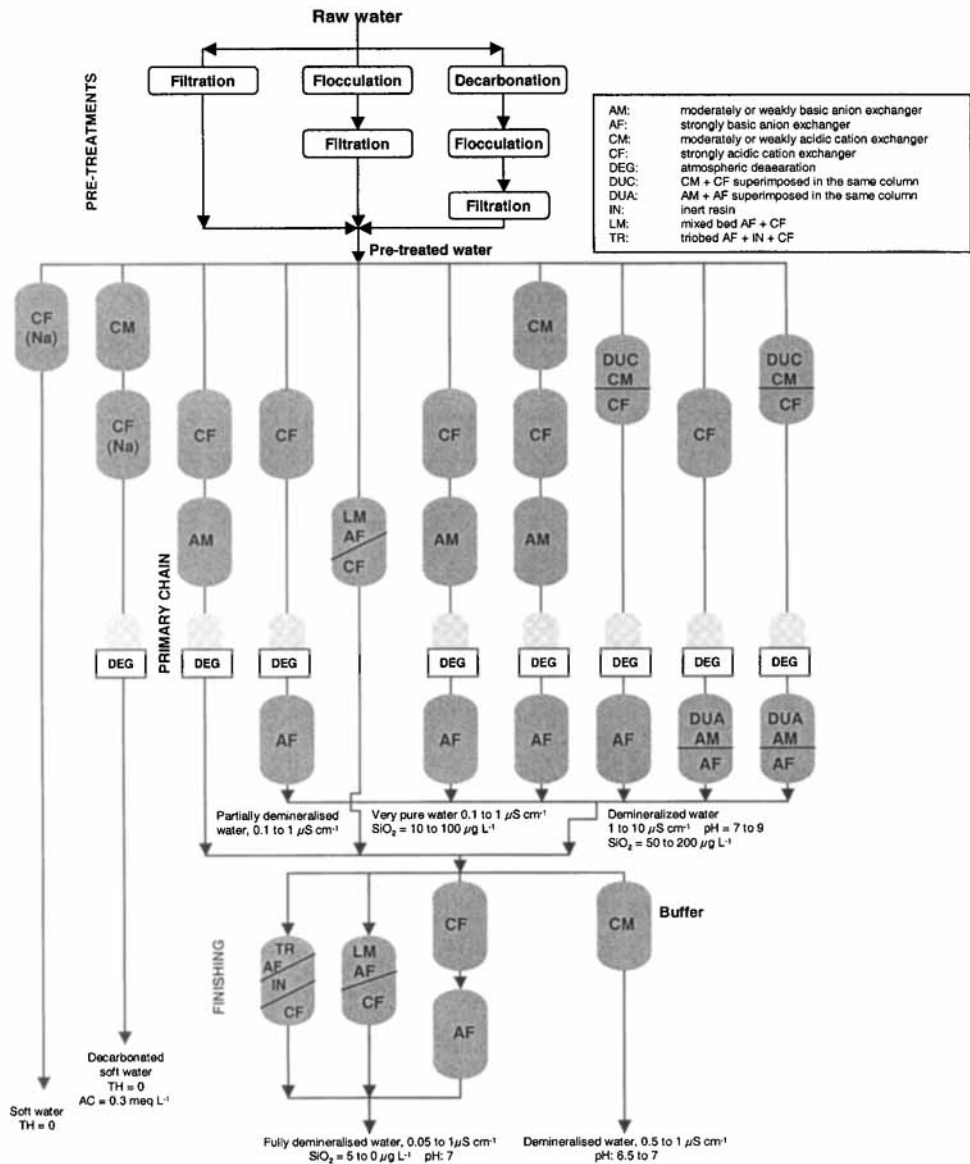
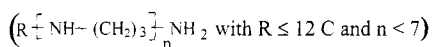


Diagram 2. Representation of the different combinations of ion exchangers (F. Dardel, Techniques de l'Ingénieur J2 784).

Appendix D

Chemical Formulae for Actives

Amines and fatty polyamines

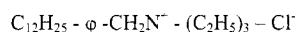


Example : octadecylamine

Quaternary ammonium salts



Example: dodecyl benzyl triethyl ammonium chloride

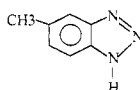


Azole derivatives

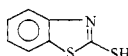
Examples : benzotriazole



tolytriazole

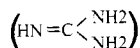


2-mercaptobenzothiazole

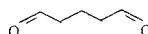


benzimidazole, 2-aminopentyl 5, ...

Long chain aliphatic guanidine derivatives

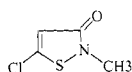


Glutaraldehyde

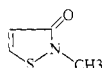


Isothiazolines

Examples : 5-chloro-2-methyl-4-isothiazolin-3-one



2-methyl-4-isothiazolin-3-one

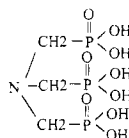


Organophosphates

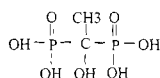
★ Phosphonates, phosphonic acid

(P-C-P or P-C-N-C-P bonds)

Examples: amino tri(methylene phosphonic acid) (ATMP)

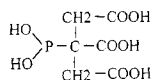


hydroxyethane diphosphonic acid (HEDP)



★ Phosphonoalkyl carboxylic acids

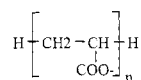
Example : phosphono butane tricarboxylic acid (PBTC)



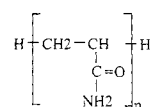
'Polycarboxylic' acrylic polymers and copolymers

(molecular weight from 500 to 10^4 g mol⁻¹)

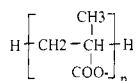
★ Polyacrylates



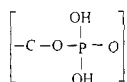
★ Polyacrylamides



* Polymethacrylates

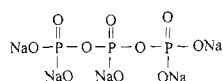


* Polyolesters, phosphonic esters of polyalcohols

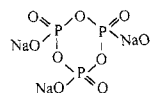
**Polyphosphates**(PPO₄) (P–O–P bonds)

*Linear

Example : Sodium tripolyphosphate
(Na₅P₃O₁₀)



*Cyclic or polymetaphosphates



Example: Sodium hexametaphosphate
(NaPO₃)

Thiocyanates

Example: methylene dithiocyanate



Glossary

Chelate	Metal ion complex in which at least one ligand is an anion with two or more complexing sites, enabling the metal ion to be enclosed like a ball in a pincher or cage.
Complex	Combination in which several apparently saturated molecules or ions are bound together in such a way that their chemical properties disappear.
Dispersant	Additive that creates or stabilises a colloidal suspension.
Wetting agent	Chemical substance capable of lowering the surface and interface tensions of liquids.
Surfactant	Soluble amphiphile molecule that reduces the surface tension of a liquid at low concentrations.